Extraction of Carboxylic Acids from Hydrocarbon Using Silica as Solid Adsorbent

by

Wan Madihah Binti Omar

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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A project dissertation of submitted to the
Chemical Engineering Programme
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Approved by,

(Dr Mohamed Ibrahim Abdul Mutalib)

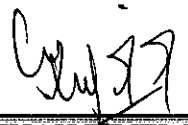
UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

May 2012

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.



WAN MADIHAH BINTI OMAR

ABSTRACT

This project has introduced a new method to extract naphthenic acid from the hydrocarbon. The method is by using silica bed immobilized with ionic liquids as a solid adsorbent to extract the naphthenic acid. In this study, four different types of ionic liquids which are EMIM DEP, BMIM DCN, BMIM OTF, BMIM $MeSO_4$ are evaluated. These ionic liquids have been immobilized to silica gel 0.063mm with 1:2 ratio which acted as solid adsorbent to extract acid from model oil. Model oil is contained of 2.7 wt% hexanoic acid and 1.0 wt% benzoic acid in dodecane. The carboxylic acid extraction mechanism is studied by performing solid phase extraction with silica immobilize with ionic liquids. The EMIM DEP immobilized silica showed highest acid removal from both model oil and capacity of EMIM DEP to extract acid is proved by multiple stages extraction with 100% removal for each stages.

ACKNOWLEDGEMENT

Firstly, I give my utmost gratitude to ALLAH the Almighty for his uncountable graces upon me and for the successful completion of this project in due course of time.

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LIST OF ABBREVIATIONS

NA	Naphthenic Acid
NAC	Naphthenic Acid Corrosion
TAN	Total Acid Number
IL	Ionic Liquids
EMIM DEP	1-ethyl-3-methylimidazolium diethyl phosphate
BMIM DCN	1-butyl-3-methylimidazolium dicyanamide
BMIM OTF	1-butyl-3-methylimidazolium trifluoromethanesulfonate
BMIM $MeSO_4$	1-butyl-3-methylimidazolium methylsulfate
HA	Hexanoic Acid
BA	Benzoic Acid
GC	Gas Chromatography

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

1.1.1 Carboxylic Acid or Naphthenic Acid Corrosion (NAC)

Naphthenic acid (NA) in petroleum industry refers collectively to the organic acids present in crude oil. The main concern of NA present in the crude oil is the corrosion problem that will affect the production cost of petroleum refining industry and ultimately affect the oil market forecast. The primary method to evaluate the corrosivity of crude is by Total Acid Number (TAN) technique which is basically an indicative of the NA content in the crude oil.TAN is milligrams of KOH required to neutralize the acidity one gram oil (Aihua Zhang, 2006).Theoretically, NA over 0.5 TAN in the feed stock and over 1.5 TAN in side cut streams is considered corrosive.

Naphthenic acid attack is a metal loss mechanism observed primarily in refinery crude, distillation and vacuum units and their equipment, for example pumps, furnaces, transfer lines, heat exchangers, condensers. This type of corrosion affects carbon and low alloy steels, stainless steels and some nickel alloys. NAC is commonly reported occurs in the range of operating temperature of 232°C to 399°C with maximum damage occurring between 288°C and 343°C when the NA is condensing. Typically, NA attack does not occur below 232°C and above 399°C as the lighter molecular weight naphthenic acid species will decompose at these temperature ranges (B. Messer, 2004).

Basically, there are three types of mechanism are proposed for NAC. For the Type I, it is due exclusively to the NA where sulfur compounds have little or no effect if they are present. Type I involves the corrosion at vacuum column which preferential vaporization and condensation of naphthenic acids that could increase TAN of condensates. This type

of condensate corrosion is directly related to content, molecular weight and also boiling point of the naphthenic acid (Ropital, 2010).

For the second type, Type II is in which sulfidation is accelerated by the presence of naphthenic acid. This type of mechanism often occurs at furnaces tubes and transfer lines which temperature, velocity and degree of vaporization gives a big influence to the rate of corrosion. The high temperature activates even small amounts of NA in oil that could increase the corrosion. While the greater amount of vaporization, the higher the velocity and the higher the corrosion would be (Ropital, 2010).

Last but not least, Type III is where the NAC is inhibited to some extent by the sulfur containing compound, hydrogen sulfide. Corrosion at the side cut piping is recognized as the Type III which the conditions of low vaporization and medium fluid velocity exist at this part of the equipment. The corrosion rate is increases as the velocity increases (Ropital, 2010)

The corrosion reaction processes are described typically by:

i. Direct acid attack on iron:

$$Fe + 2RCOOH \leftrightarrow Fe(RCOO)_2 + H_2$$

ii. Attack of iron naphthenate by H_2S (this reaction regenerates naphthenic acid which can cause further corrosion)

$$Fe(RCOO)_2 + H_2S \leftrightarrow FeS + 2RCOOH$$

1.2 PROBLEM STATEMENT

Due to developing technology and higher demand in oil and gas production throughout the world, many methods have been applied in the petroleum refining industry in order to solve the NAC problem. One of the current industrial methods is by practicing dilution or caustic washing by blending a high TAN crude oil feedstock with a low TAN crude or fraction. This crude oil blending method can reduce the average TAN by about 0.2 to 0.5 mg KOH/g. If the TAN is not too high, the sulfur content can be increased provided that this does not disturb the downstream processing operations (Ropital, 2010).

The other NAC prevention is the addition of corrosion inhibitor which is a substance that when added in a small concentration to an environment effectively reduces the corrosion rate of a metal exposed to that environment. Formulations of this inhibitor are based on phosphate ester, thiophosphorated and more recently sulfur compounds are currently proposed as the corrosion inhibitor (Ropital, 2010).

Another mitigation options for NAC prevention is by upgrading metallurgy of the construction material. It is important to choose the metallurgy adapted to the acidity of the feedstocks that are to be treated. Materials of construction with containing higher chrome and molybdenum offer enhance corrosion resistance. For instance, 316SS (18% Cr and 2% Mo min.) and 317 SS (18% Cr with 3% Mo min.) that exhibit the greatest corrosion resistance (Ropital, 2010).

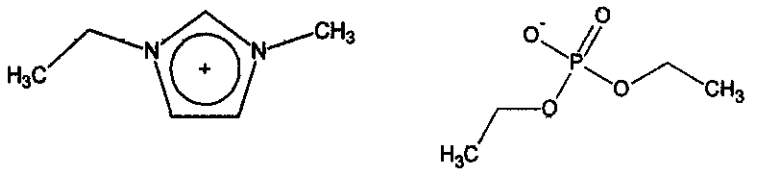
With all these current methods, it is seen very significant to carry out another method that has possibility to deal with NAC problem as a support method to enhance the corrosion prevention technology. Thus, in this study research ionic liquid-functionalized silica is proposed as an adsorbent to extract carboxylic acid or naphthenic acid from hydrocarbon. Ionic liquids that have been immobilized on silica particles have a great potential in NAC mitigation as they provide new sorbents with interesting properties for analytical chemistry of extraction and separation process.

1.3 OBJECTIVES AND SCOPE OF STUDY

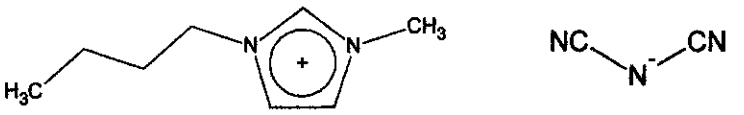
The scope of this project will be focusing on the NA extraction mechanism using silica bed immobilized with ionic liquids. The objectives of this project that have to be achieved are:

1. To immobilize ionic liquid onto silica surfaces.
2. To determine the characterization of the immobilized silica.
3. To conduct an extraction process using model oil containing NA acid.
4. To determine the NA extraction mechanism.

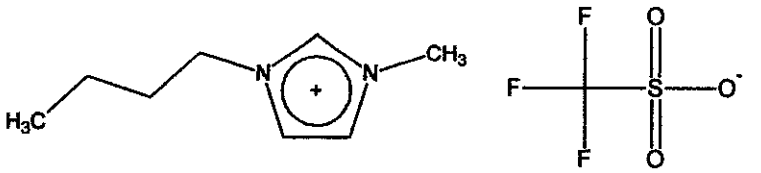
Four types of ionic liquids under studied are:



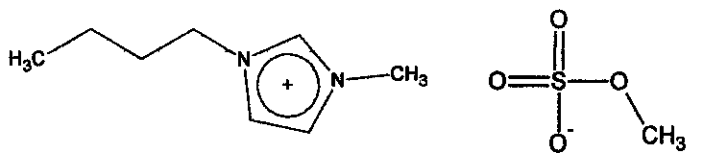
1-ethyl-3-methylimidazolium diethylphosphate



1-butyl-3-methylimidazolium dicyanamide



1-butyl-3-methylimidazolium trifluoromethanesulfonate



1-butyl-3-methylimidazolium methylsulfate

CHAPTER 2

LITERATURE REVIEW

2.1 CRUDE OIL BLENDING

Blending is the most common and preferred method of reducing the severity of high temperature corrosion in crude oil refining systems. Other than to prevent NAC, this method purpose is to increase the sale price or process ability of a lower grade crude oil. It is accomplished by blending the high TAN crude oil with the low TAN crude oil. This technique reduces the overall TAN value to an acceptable low rate level of corrosive attack. Crude oil blending could also be carried out with the high sulfur crudes to decrease corrosion of the equipment by forming a protective iron sulfide film. The iron sulfide film on the metal surfaces potentially offers protection against naphthenic acid attack (Shalaby, 2009).

2.1.1 On-line Blending

In on-line blending method two or more components are injected from separate pipelines and are mixed in a single line. In this method it is necessary to ensure adequate mixing. It is requires some type of in-line static mixer or mechanical mixing device as the use of piping elements alone may not provide adequate mixing. The efficiency of this method will depend upon the resulting stream's Reynolds number, the type and number of piping elements, and also the time allowed for mixing (MacDougall, 2007).

Often in on-line blending only the smaller stream's flow rate is varied whereas the larger is kept constant. The ratio of the two streams depends upon a controlling parameter that is monitored downstream of the common injection point. The monitoring can be performed automatically using on-line analytical equipment or manually by collection of samples. The injection rate of the smaller stream is based upon the sample analysis. An improvement in this application would be a ratio control system where the flow rates of

both streams are measured and the analysis from the manual sample determinesthe setpoint for the ratio. This is beneficial where the flow rate of the larger stream tends to vary (MacDougall, 2007).

2.1.2 Tank Blending

For the tank blending method, it is basically by mixing two components based on a recipe approach where the components are added in a common tank. The challenge of this method is to achieve homogeneous blending and the blending is depends upon the ratios of the two components, similarity in physical properties, size of tank, number of tank mixers and mixing time. It is preferable to add both components simultaneously as the tank is filled rather than filling with one at a time. If the only available option is to fill with one at a time, the component with the lowest concentration is added first (MacDougall, 2007).

The crude oil blender for the tank blending method normally use viscosity and density trim control systems as the crude oil feed stocks used for blending often vary in quality. The control system is based on the recipe approach where the crude oil blender is started at the required flow rate and set of component ratio. However there is upside of the recipe approach as it is potentially less homogeneity and less certainly in meeting proper specification as there is no process feedback until the blending is complete. Thus, a density or viscosity analyser is installed at a homogeneous point in the blender header that will generate a control signal, which is used to continually optimise the blended product by adjusting the component ratio. This ensures that the blended product remains as specified at all times during the batch. Figure 2.1 below is one of the crude oil blenders with self-learning control algorithms that corresponds to changes in process conditions or feedstock quality (MacDougall, 2007).

Figure 2.1 Crude oil blender

2.2 CORROSION INHIBITOR

Addition of corrosion inhibitors is one of the common methods to control both general and pitting corrosion of oil and gas pipelines. Injection of corrosion inhibitors may provide adequate and economic protection if it is closely monitored and used for specific fractions that are known to be particularly severe or that fluctuate with feedstock quality. One of the advantages of corrosion inhibitor is it can be implemented or changed without disrupting a process. Experience with inhibitors used to mitigate high temperature crude oil corrosion is limited but growing rapidly. The inhibitor does not completely stop the corrosion reaction but it eliminates more than 99% of the metal losses that would occur if the inhibitor were not present (Denis Brondel, 1994).

The type and amount of inhibitor used not only depends on the acid and its strength but also on the metal it is protecting, the working temperature range and the protection time desired. Specific corrosion inhibitors are environmentally compatible which is effective in H_2S environments, effective in high chrome steel and on special steel alloys. These inhibitors may be used at temperatures approaching 260°C which is in the temperature range of NAC. One of the inhibitor injections is by using capillary tube. The chemical inhibitors are absorbed onto a metal surface from solution to protect against corrosion (Denis Brondel, 1994).

The protective films that are formed in the inside of the capillary tube such as iron sulphide and iron carbonate scales provide protective coatings to the corrosion products

when H_2S and CO_2 are present. These protective films could slow corrosion by increasing anodic and cathodic polarization, reducing diffusion of ions to the metal surface, increasing the electrical resistance at the metal electrolyte interface and by increasing the hydrogen over voltage. The voltage is required to remove hydrogen and prevent the corrosion process (Denis Brondel, 1994).

The corrosion inhibitor can be divided into two broad categories, phosphorus containing and no-phosphorus inhibitor.

2.2.1 Phosphorus Inhibitor

Phosphorus based compounds are known to be effective in naphthenic acid corrosion control. These inhibitors could form a protective scale or barrier on the metal which prevents or slows the diffusion of acids to the active metal. These inhibitors are relatively volatile and exhibit fairly narrow distillation ranges. The phosphorus-containing formulations are generally more effective than the non-phosphorus but bring with them the concern about poisoning downstream catalysts that used to treat crude oil (Shalaby, 2009).

2.2.2 Non-phosphorus Inhibitor

Sulfonated alkyl-substituted phenol is one of the non-phosphorus inhibitor that is a very effective NAC inhibitor when present in very low concentrations in a hydrocarbon fluid or stream containing naphthenic acid. It has been discovered that this inhibitor is not a catalyst poison as the sulfonated alkylphenol is sulfur-based and will not impair the function of conventional stationary bed catalysts like phosphorus-based corrosion inhibitors can. Hence, it could provide a longer catalyst life in hydrotreaters and hydrocracking units (Babaian-Kibala, 1993).

2.3 METALLURGY UPGRADE

It is important to select a good material construction which is capable to resist acid corrosion of the feedstock that is to be treated. The selection of materials of construction has a significant impact on the operability, economics and reliability of refining units. For this reason, materials selection should be a cooperative effort between the materials engineer, plant operations and maintenance personnel. A good material must not only be suitable for normal process conditions but must also capable to handle transient conditions that encountered during start-up, shutdown, emergencies or extended standby(Shalaby, 2009).

The effective metallurgy upgrade is by choosing the material of construction that has higher chrome and molybdenum that can enhance corrosion resistance. For the case where TAN values are low and sulfur is the primary corrodant, 5 to 12% Cr steels are usually used. For severe conditions of sulfidic attack that is created by temperature and sulfur content, a minimum of 9% Cr is typically preferred. For the TAN above 0.5 and above 1.5 in the atmospheric column, it is preferable to use higher alloys, such as type 316SS (18% Cr and 2% Mo min.) or type 317SS (18% Cr and 3% Mo min.) which have a great naphthenic acid corrosion resistance. However, the drawback by choosing these types of alloys is they are quite expensive and then directly would increase the refining cost (Shalaby, 2009).

2.4 IONIC LIQUID-IMMOBILIZED SILICA

In the recent studies, ILs that have been immobilized on silica particles provide new sorbents with interesting properties for analytical chemistry of extraction and separation process. Although once the IL immobilized on a surface will lose its liquid state, the other unique properties such as low volatility and its polarity supporting non-polar and ionic interactions are maintained. They act as low-polarity phases for non-polar compounds and in the opposite manner for compounds bearing strong proton-donor

groups. This behaviour depends on the separation mechanism that involves multiple interactions such as electrostatic, hydrophobic and π. These new sorbents have been successfully applied as stationary phases in liquid chromatography, gas chromatography and as sorbents in SPE (Lorena Vidal, 2012).

Researchers have published a study on ionic liquid-functionalized silica for selective solid-phase extraction of organic acids, amines and aldehydes at different pHs. Three IL functionalized silica materials which are imidazolium, N-methylimidazolium and 1-alkyl-3-(propyl-3-sulfonate) imidazolium have been synthesised and applied in SPE. The effect of pH stability has been investigated to clarify the retention mechanisms of the IL materials studied and also the hydrophobic and π interactions and hydrogen bonding. These three IL-functionalized silica materials characterization were compared with two commercial extraction materials, silica-based strong anion exchange (SAX) and polymer-based mixed-mode anion exchange and reverse-phase (MAX) proved that the IL-silica materials to offer different selectivity and better extraction efficiency than SAX for aromatic compounds(Lorena Vidal, 2012).

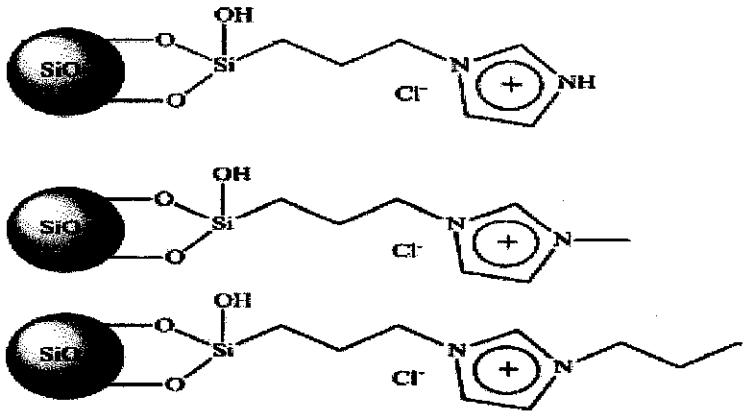


Figure 2.2 IL-modified silica sorbents used in solid phase extraction

CHAPTER 3

METHODOLOGY

Before conducting this project, it is necessary to understand the basic principles and concepts that involved in the process. Properties of ILs, immobilization of IL onto silica surfaces and handling all the chemicals based on the MSDS will be studied before starting the experiment in the laboratory. All of these required to do a research and literature review by getting resources from the library, online journal and information from the internet.

3.1 METHODOLOGY OF THE PROJECT

3.1.1 Immobilization of Ionic Liquid with Silica

i. Four types of ionic liquids under studied were, 1-ethyl-3-methylimidazolium diethyl phosphate (EMIM DEP), 1-butyl-3-methylimidazolium dicyanamide (BMIM DCN), 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BMIM OTF), 1-butyl-3-methylimidazolium methylsulfate (BMIM $MeSO_4$).It is done by synthesis 1-butylimidazole, $C_7H_{12}N_2$(excess 0.075 mol) with (3-chloropropyl) triethoxysilane, $C_9H_{21}ClO_3Si$ (0.07 mol). The solvent that can be used is about 15 mL toluene.

ii. These ionic liquids have been immobilized with calcined commercial silica gel 0.063mm with 1:2 ratios (g). 40 mL of toluene added as a solvent.

iii. The solution has been mixed using water bath shaker for 24 hr. The reaction was then stopped and the toluene solvent has been evaporated by using rotary evaporator.

iv. The ionic liquid immobilize silica was dried overnight at 60°C.

Table 3.1 Actual ratio of ionic liquids and silica

1)	EMIM DEP = 1.5195 g Silica = 3.0005 g
2)	BMIM DCN = 1.5340 g Silica = 3.0017 g
3)	BMIM OTF = 2.01 g Silica = 3.0048 g
4)	BMIM $MeSO_4$ = 1.5220 g Silica = 3.0098 g

Figure 3.1 Immobilization of ionic liquid onto silica surfaces

3.1.2 Preparation of Model Oil

i. 2.7 wt% concentration of hexanoic acid in dodecane has been prepared.

ii. Hexanoic acid = 0.8123 g

Dodecane = 29.2507 g

$$\frac{0.8123}{0.8123 + 29.2507} \times 100 = 2.7wt\%$$

iii. 1.0 wt% concentration of benzoic acid in dodecane has been prepared.

iv. Benzoic acid = 1.5 g

Dodecane = 148.55 g

$$\frac{1.5}{1.5 + 148.55} \times 100 = 1.0wt\%$$

3.1.3 Preparation of Column

i. Below compounds have been added layer by layer:
   0.2 g of glass wool
   0.5 g of sea sand
   1 g of IL immobilized silica (dry prior use)

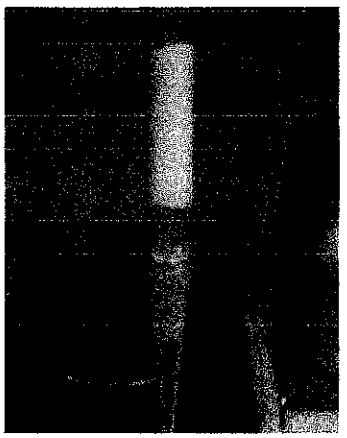


Figure 3.2 Extraction column

3.1.4 Extraction of Carboxylic Acids from Model Oil

i. 5 g of model oil has been eluted into the column.
ii. The collected eluted model oil at the bottom has been tested for acid content using gas chromatography.

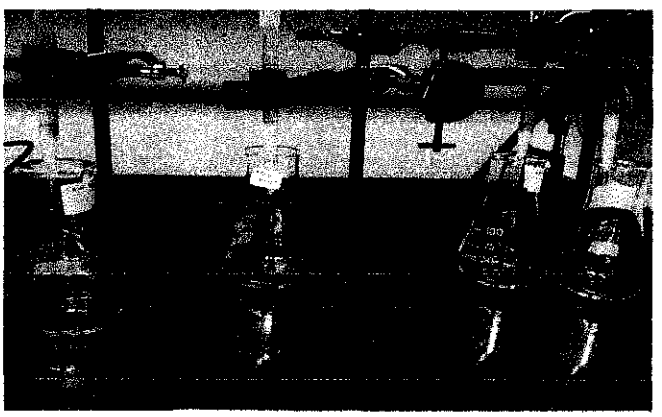


Figure 3.3 Extraction for four types of ionic liquids immobilized silica

Table 3.2 Actual extraction data for hexanoic acid extraction

1)	BMIM DCN functionalized silica = 1.0065 g glass wool = 0.2014 g model oil = 5.0038 g
2)	EMIM DEP functionalized silica = 1.0058 g glass wool = 0.2010 g model oil = 5.0890 g
3)	BMIM OTF functionalized silica = 1.0058 g glass wool = 0.2014 g model oil = 5.0610 g
4)	BMIM $MeSO_4$ functionalized silica = 1.0158 g Glass wool = 0.2002 g Model oil = 5.0100 g

Table 3.3 Actual extraction data for benzoic acid extraction

1)	BMIM DCN functionalized silica = 1.0060 g glass wool = 0.2028 g model oil = 5.0157 g
2)	EMIM DEP functionalized silica = 1.0040 g glass wool = 0.2015 g model oil = 5.0083 g
3)	BMIM OTF functionalized silica = 1.0040 g glass wool = 0.2030 g model oil = 5.0280 g
4)	BMIM $MeSO_4$ functionalized silica = 1.0134 g Glass wool = 0.2010 g Model oil = 5.0039 g

3.1.5 Multiple Stages Extraction

i. The same column has been eluted with fresh model oil at five stages and every oil are collected separately and has been analyzed with gas chromatography.

3.1.6 Preparation of Standard Model Oil for Gas Chromatography Analysis

Table 3.4 Standard of model oil (Hexanoic Acid)

Standard	Theoretical wt% of Hexanoic Acid	Actual wt% of Hexanoic Acid
1	0.5	0.5137
2	1.0	1.0472
3	1.5	1.5533
4	2.0	2.0150
5	2.5	2.5191
6	3.0	3.0600

Table 3.5 Standard of model oil (Benzoic Acid)

Standard	Theoretical wt% of Benzoic Acid	Actual wt% of Benzoic Acid
1	0.2	0.2178
2	0.4	0.4085
3	0.6	0.6197
4	0.8	0.8096
5	1.0	1.0840
6	1.2	1.2486

3.1.7 Cross Solubility Analysis

i. Collected dodecane has been diluted with 15 mL deionized water (500 rpm, 30 minutes).
ii. Left for 1 hour for separation water layer.
iii. Control experiment: 1 mL EMIM DEP has been dissolved in 100 mL deionized water. EMIM DEP peak has been defined at 4.72 min.

3.2 GANTT CHART AND KEY MILESTONES

Gantt chart for activities planned along for this final year projects first and second semester are shown in Table 2 and Table 3.

Table 3.6 Gantt chart for final year project first semester (FYP I)

No	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Topic Selection															
2	Research About Topic															
3	Complete Literature Review															
4	Submission of Extended Proposal															
5	Proposal Defence															
6	Identification of Materials															
7	Development of Methodology															
8	Submission of Interim Report															

Mid-Semester Break

Table 3.7 Gantt chart for final year project second semester (FYP II)

No	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	Immobilization IL-Functionalized Silica																
2	Characterization of Immobilized Silica																
3	Extraction Process of NA Acid																
4	Submission of Progress Report																
5	Data Analysis and Report																
6	Pre-EDX																
7	Submission of Dissertation and Technical Paper																
8	Oral Presentation																
9	Submission of Project Dissertation (hardbound)																

CHAPTER 4

RESULTS AND DISCUSSION

4.1 GAS CHROMATOGRAPHY ANALYSIS

Sample that containing model oil collected from extraction process for each different type of ionic liquids have been analysed by using gas chromatography (GC) in order to determine carboxylic acids content after extraction. From the calibration curves obtained from GC analysis, concentration of carboxylic acids in dodecane for each sample could be determined.

4.1.1 Hexanoic Acid Model Oil

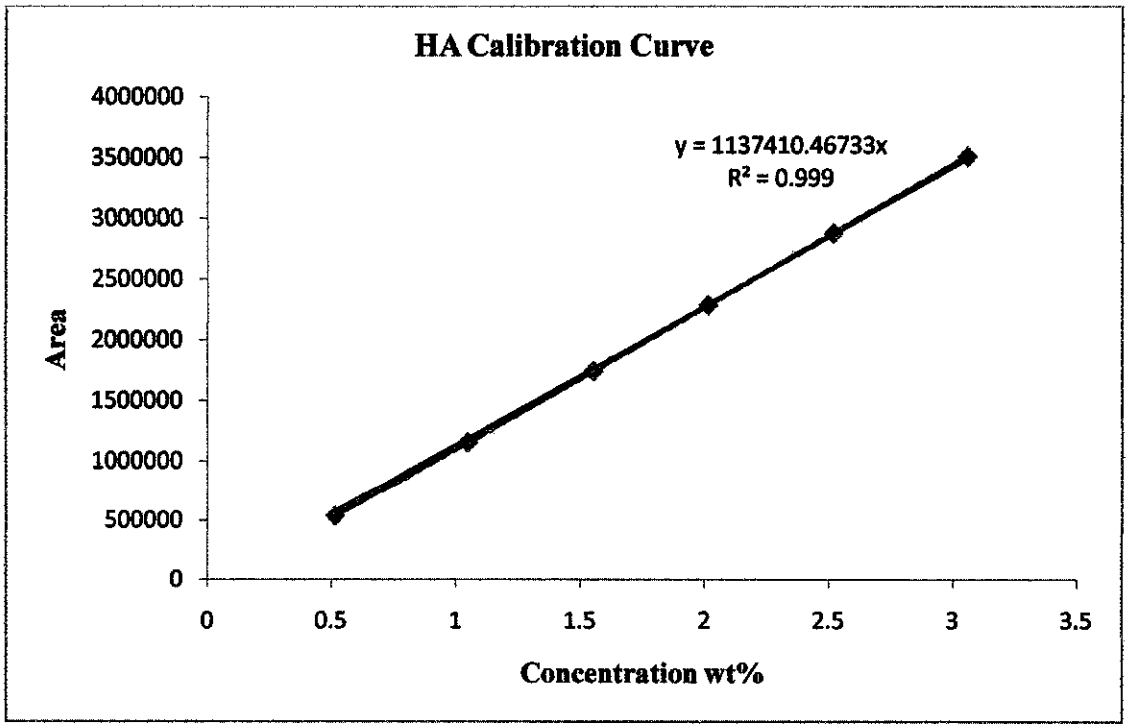


Figure 4.1 Hexanoic acid calibration curve

Figure above shows that the calibration curves for hexanoic acid from the standards model oil. Results of area from GC for the unknown concentration of hexanoic acid in the collected eluted model oil will be calibrated with this graph. Results for each sample of model oil from extraction process are:

Table 4.1 Concentration of HA after extraction

Sample	Area	Concentration (wt%)
EMIM DEP	-	0
BMIM DCN	717291.25	0.631
BMIM OTF	2340882.40	2.058
BMIM $MeSO_4$	1576890.22	1.386

Example of calculation for sample BMIM DCN;

$$y = 1137410.46733x$$

$$y = 717291.25$$

$$x = \frac{717291.25}{1137410.46733} = 0.631 \text{ wt\%}$$

Table 4.2 HA Removal %

Sample	Initial HA Concentration (wt%)	Final HA Concentration (wt%)	HA Removal (%)
EMIM DEP	2.69	0	100
BMIM DCN	2.69	0.631	76.54
BMIM OTF	2.69	2.058	23.49
BMIM $MeSO_4$	2.69	1.386	48.48

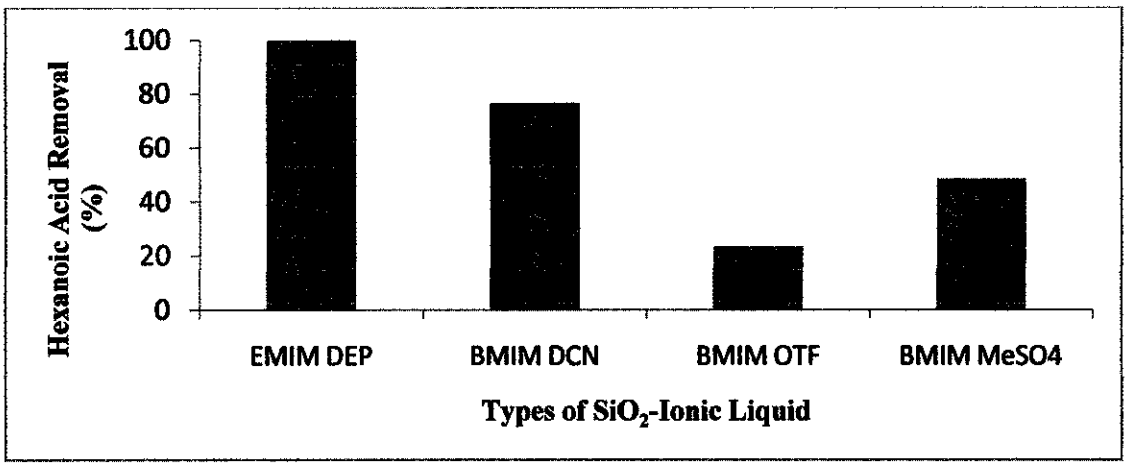


Figure 4.2 Hexanoic acid extraction

Calculation of HA Removal %;

$$= \frac{initial - final\ concentration}{initial} \times 100\%$$

From the results obtained above, EMIM DEP immobilized silica has extracted 100 % of hexanoic acid from dodecane compared with others type of ionic liquid immobilized silica. An anion exchange interaction occurred between EMIM DEP and carboxylic acids as EMIM DEP has hydrogen bond donor and hydrogen bond acceptor that made it tends to extract -COOH molecule. In order to determine the capacity that IL immobilized silica can extract the hexanoic acid, multiple stages extraction is conducted for EMIM DEP immobilized silica only based on the single stage extraction results.

Table 4.3 HA removal (%) multiple stages

Stage	Initial HA Concentration (wt%)	Final HA Concentration (wt%)	HA Removal (%)
1	2.69	0	100
2	2.69	0.5130	80.93
3	2.69	2.0574	23.52
4	2.69	2.4498	8.93
5	2.69	2.4565	8.68

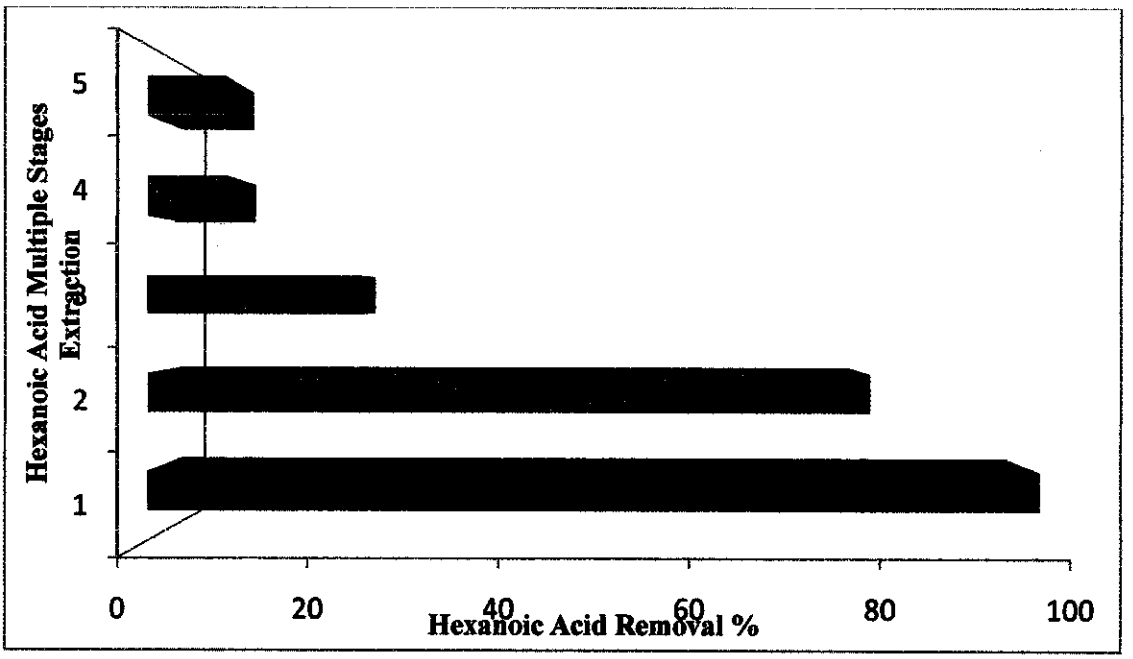


Figure 4.3 Hexanoic acid multiple stages extraction

Based on the results above, HA removal is decreasing from first to fifth stages extraction. This is due to its dipole-dipole interaction forces between the positive charge of IL and negative charge of carboxylic acids are getting weaker as the IL saturated in the extraction column when the stages increasing.

4.1.2 Benzoic Acid Model Oil

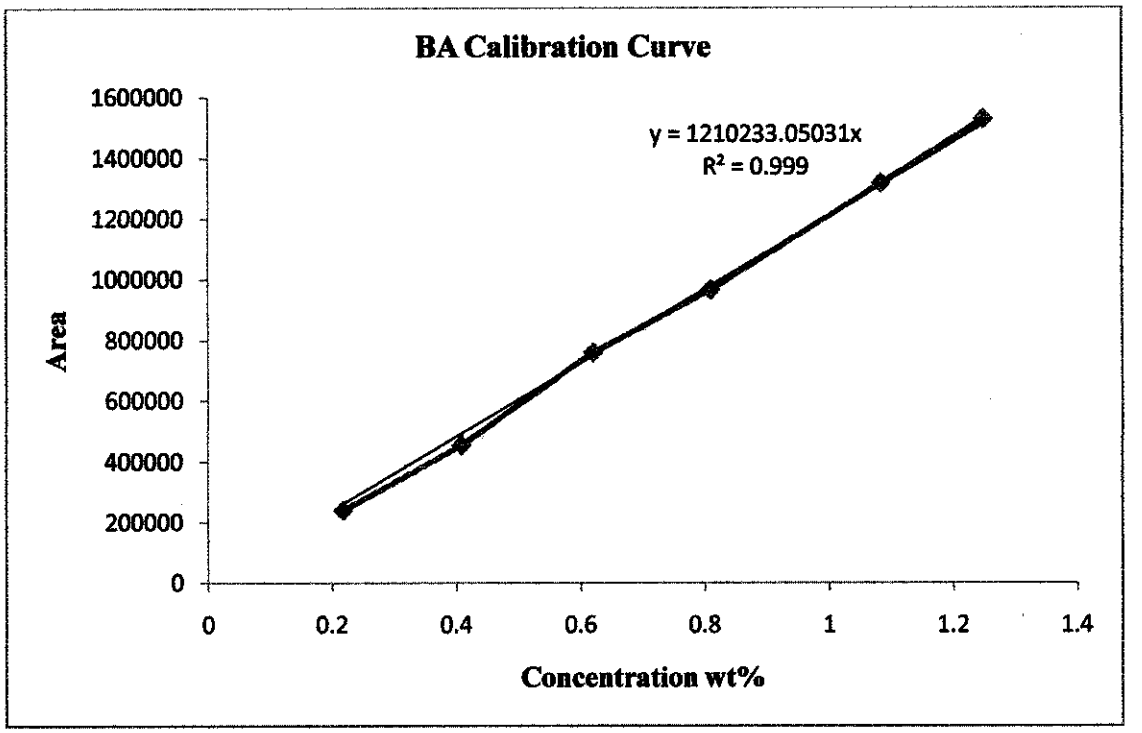


Figure 4.4 Benzoic acid calibration curve

Figure above shows that the calibration curves for benzoic acid from the standards model oil. Results of area from GC for the unknown concentration of benzoic acid in the collected eluted model oil will be calibrated with this graph. Results for each sample of model oil from extraction process are:

Table 8 Concentration of BA after extraction

Sample	Area	Concentration (wt%)
EMIM DEP	-	0
BMIM DCN	-	0
BMIM OTF	-	0
BMIM $MeSO_4$	-	0

Table 9 BA removal %

Sample	Initial BA Concentration (wt%)	Final BA Concentration (wt%)	BA Removal (%)
EMIM DEP	1.0	0	100
BMIM DCN	1.0	0	100
BMIM OTF	1.0	0	100
BMIM $MeSO_4$	1.0	0	100

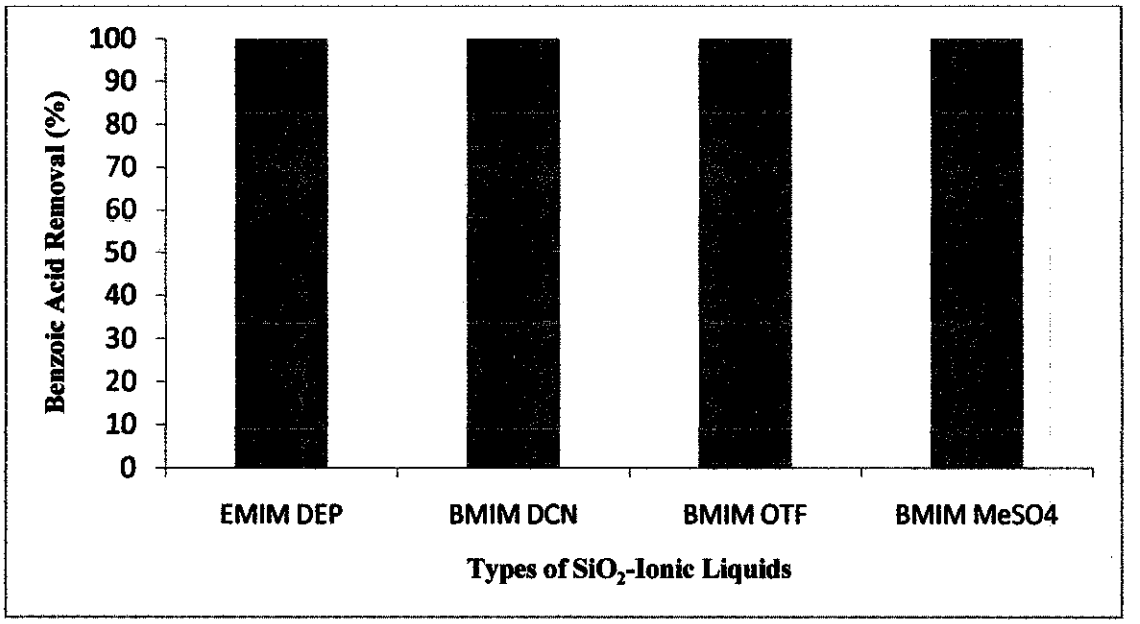


Figure 4 Benzoic acid extraction

For benzoic acid extraction, all types of IL immobilized silica has extracted 100 % of carboxylic acid from dodecane. This is due to an aromatic ring in benzoic acid molecule structure and also in imidazole structure of IL which gives high interaction between the molecules (pi interaction). The results are same applied for the multiple stages extraction which determined that 100% of acid removal for the five stages of extraction with EMIM DEP immobilized silica.

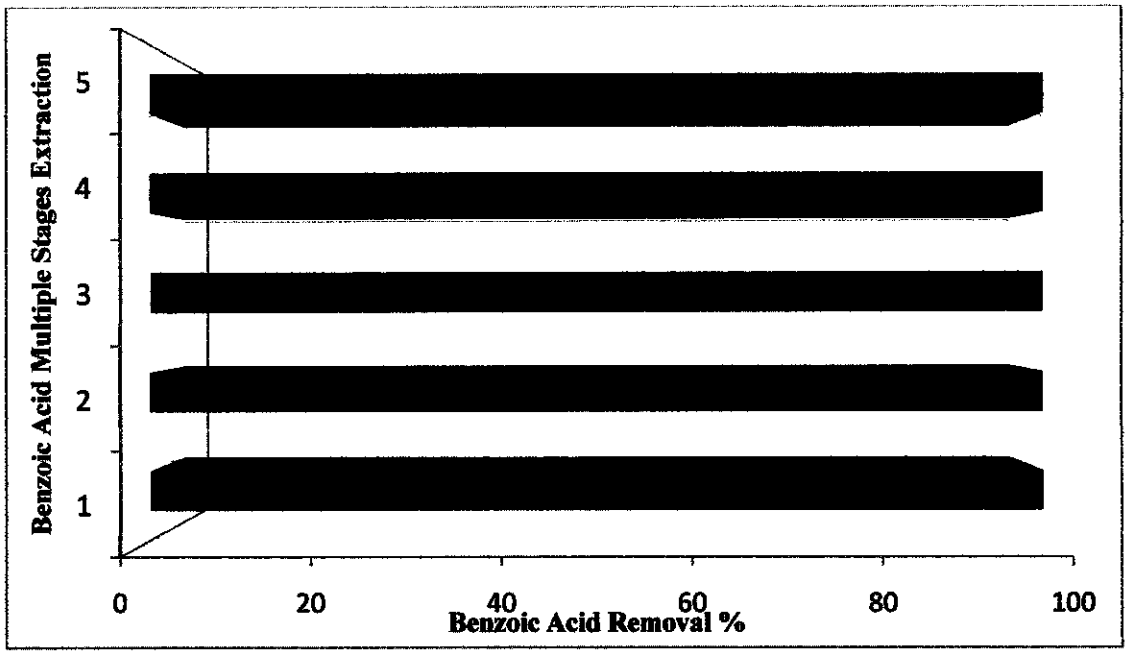


Figure 5 BA multiple stages extraction

Cross solubility of EMIM DEP in dodecane layer at fifth stages extraction is investigated using 850 Professional Ion Chromatography Metrohm Switzerland. The control experiment is compared with back extraction with water and the results for both model oil showed that there is no EMIM DEP in the solution. Thus, EMIM DEP leeching did not occur even after five multiple stages of extraction was conducted.

4.2 FOURIER TRANSFORM INFRARED (FTIR) ANALYSIS

In order to confirm the immobilization reaction, FTIR spectra of ionic liquid immobilized silica and commercial silica gel were compared between 650 and 4000 cm^{-1}. The bond in the range 3200-3500 cm^{-1} was mainly assigned to stretching vibrations of the O-H bonds of silanol groups. In the spectrum of ionic liquid immobilized silica, a characteristic frequency between 2800-3200 cm^{-1} was attributed to the C-H stretching of the tetrahedral carbon, which confirmed the anchoring of the organic molecule onto the silica surface. Frequency range between 1000-1300 cm^{-1} also proved the possible structure of silica in ionic liquid immobilized silica.

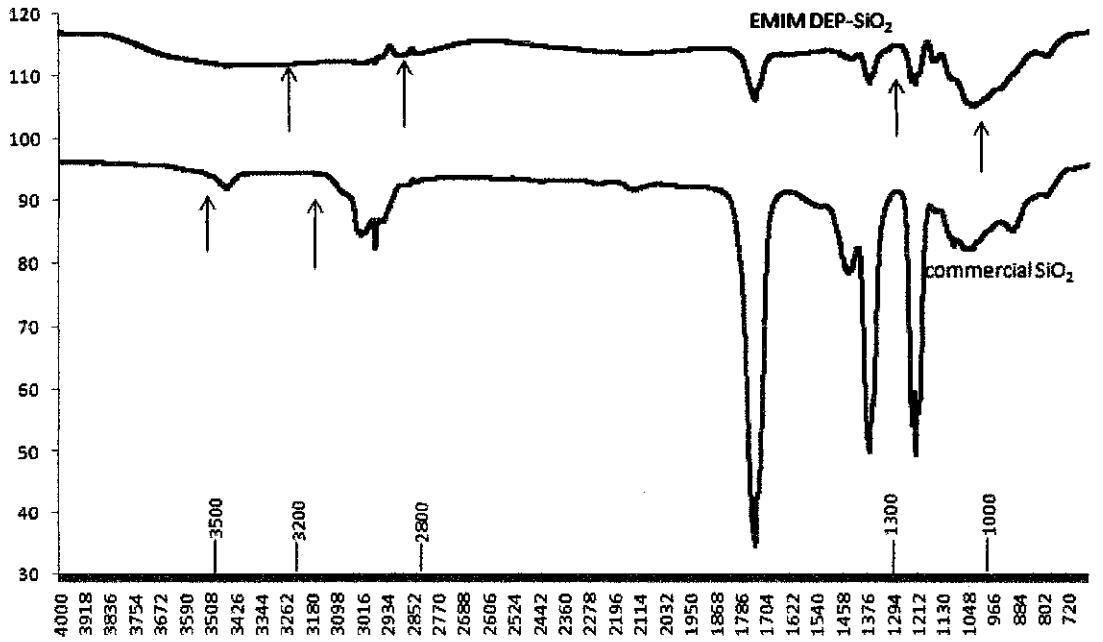


Figure 6 EMIM DEP-SiO_2 FTIR Spectrum

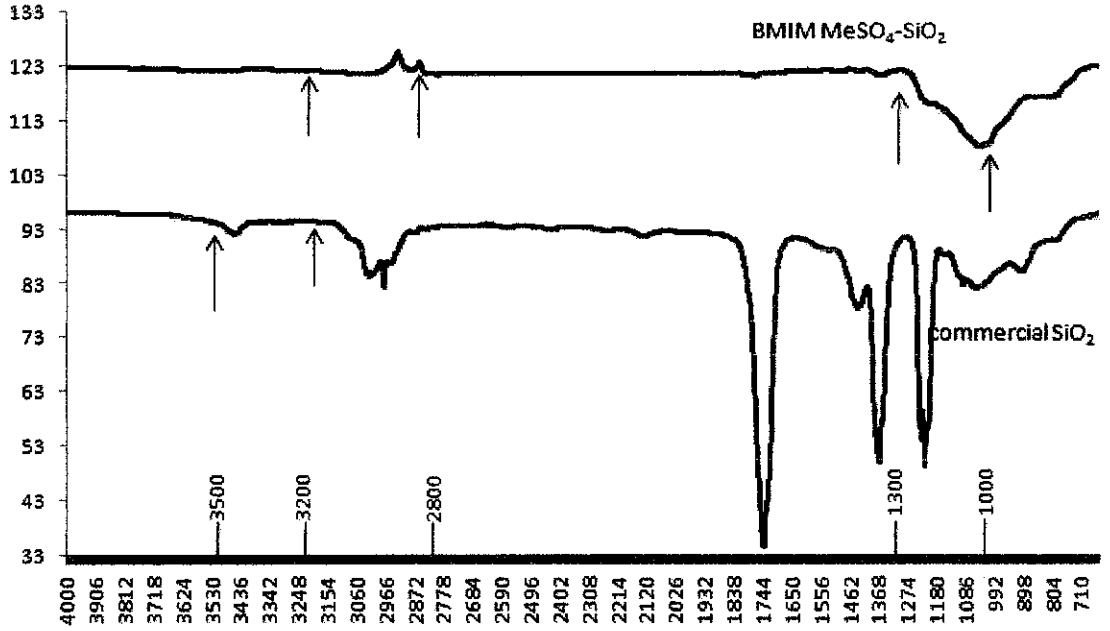


Figure 7 BMIM $MeSO_4$-SiO_2 FTIR Spectrum

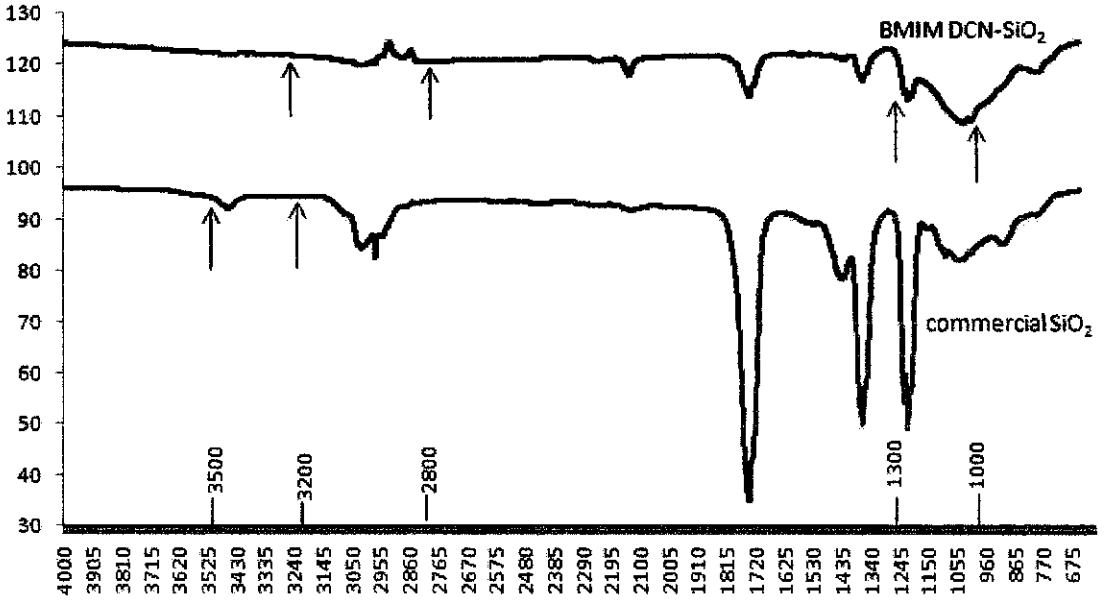


Figure 8 BMIM DCN-SiO_2 FTIR Spectrum

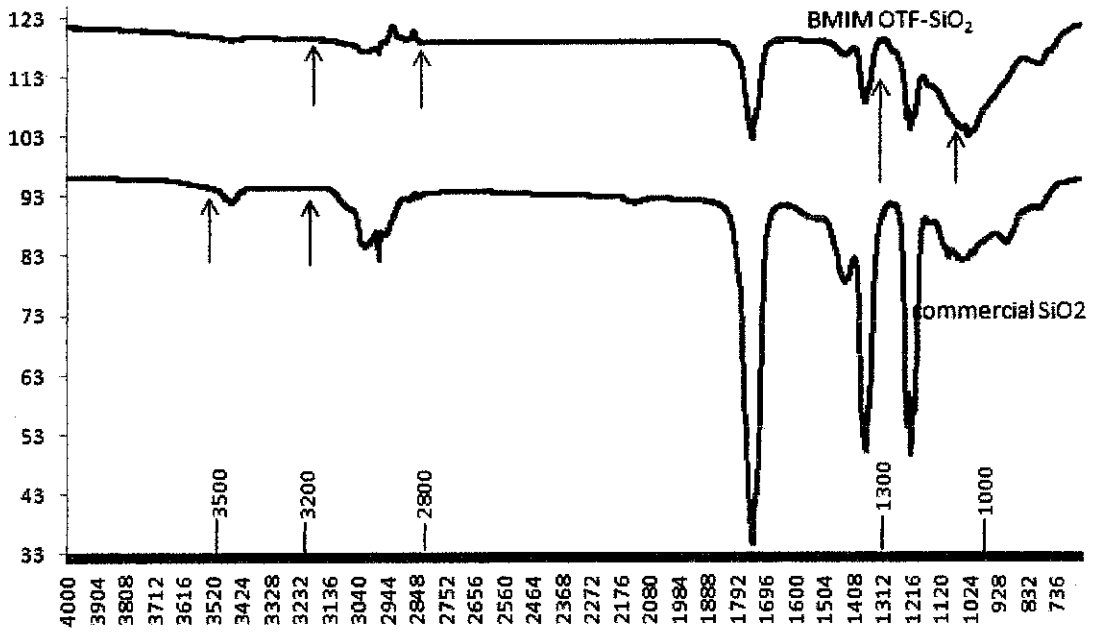


Figure 4.10 BMIM OTF-SiO_2 FTIR Spectrum

4.3 ENERGY –DISPERSIVE X-RAY SPECTROSCOPY (EDX) ANALYSIS

EDX analysis is used to study the overall chemical composition in the ionic liquid immobilized silica. The EDX spectrum of silica before immobilization presented the characteristic peaks assigned to the Si, O and C only. For immobilized silica with ionic liquids there are other elements presented in EDX measurement which is for EMIM DEP there is P (phosphate) element presence. For BMIM OTF, the result shows the presence of S and F element that corresponds to the chemical formulation of that ionic liquid.

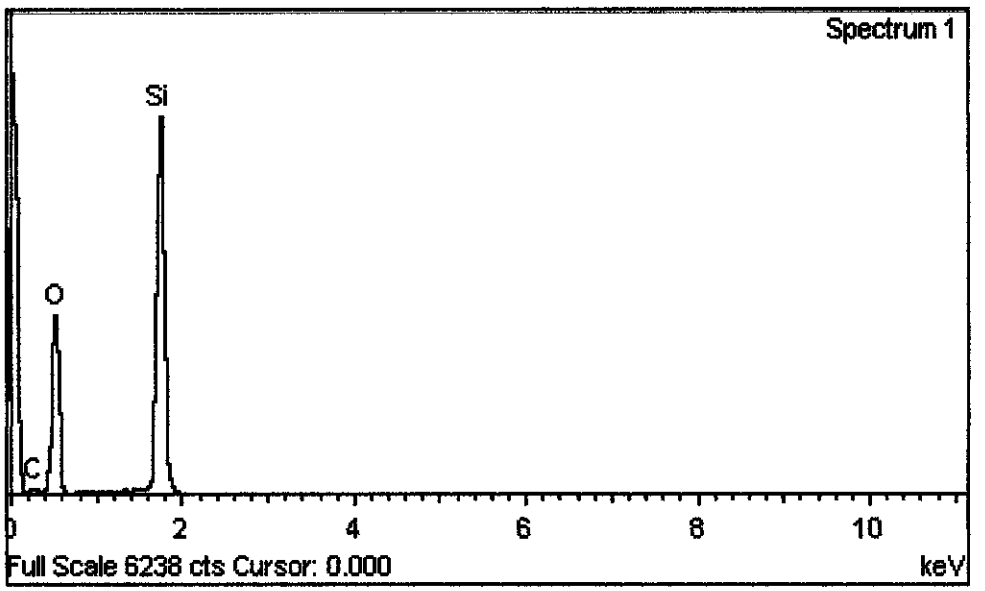


Figure 4.19 EDX Spectrum for Commercial Silica 0.063 mm

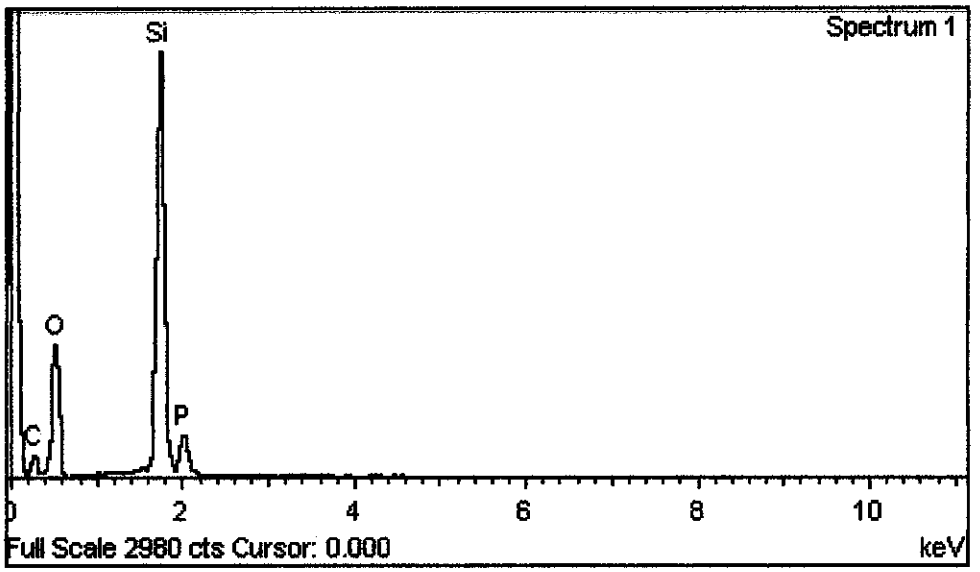


Figure 10 EDX Spectrum for EMIM DEP-SiO_2

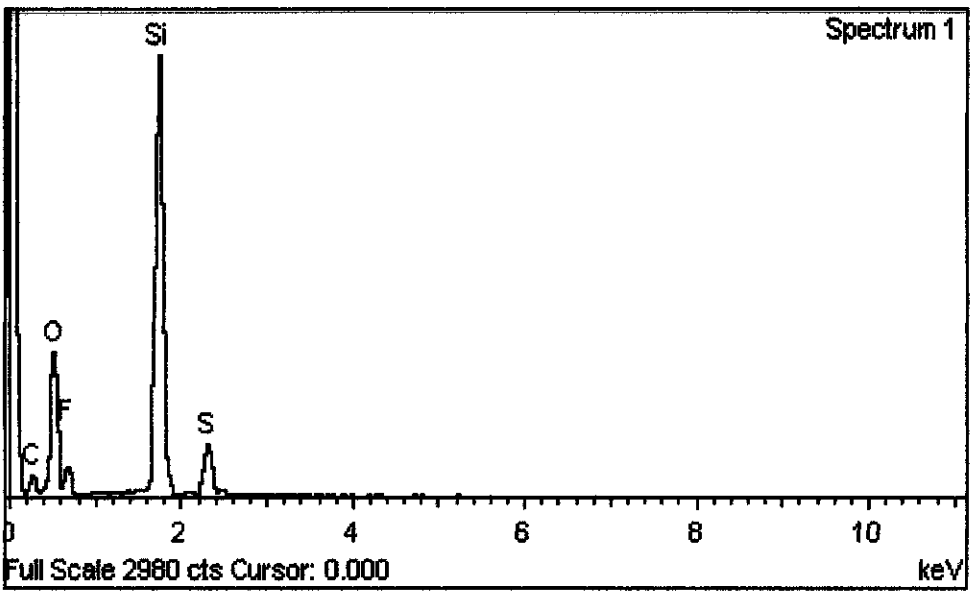


Figure 11 EDX Spectrum for BMIM OTF-SiO_2

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

This study shows that silica bed immobilized with ionic liquids can act as a solid adsorbent to extract carboxylic acids. Four types of ionic liquids have been successfully immobilized with silica. The FTIR and EDX analyses proved the presence of the IL onto silica surfaces. Extraction efficiencies for all silica bed immobilized with ionic liquids have been analysed by using GC which has shown that these IL are potential to be used as an acid extractor. Based on the results obtained, EMIM DEP immobilized silica displayed the highest extraction efficiency for both model oil compared with other types of IL. The capacity of EMIM DEP immobilized silica to extract the carboxylic acids was determined by multiple stages extraction which reveals 100% of acid removal at every stage. The EMIM DEP also did not leech to the extraction product even after five multiple stages which were proved by Ion Chromatography analysis.

5.2 RECOMMENDATIONS

For future study, there are definitely a lot of improvements that can be done to improve this project study that could benefit the oil and gas industry. Such improvements include:

- Vary the parameter for column height to improve the study of extraction mechanism.
- Immobilize IL with different size of silica gel.
- Vary the ratio of the IL and silica for the immobilization.

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Y. Duan, S. P. (2011). A Study on the Deacidification of High-Acidity Crude Oil by Combined Solvents. *Petroleum Science and Techonology, 29* , 1000-1008.

APPENDIX A – GAS CHROMATOGRAPHY

Hexanoic Acid Extraction (Single Stage):

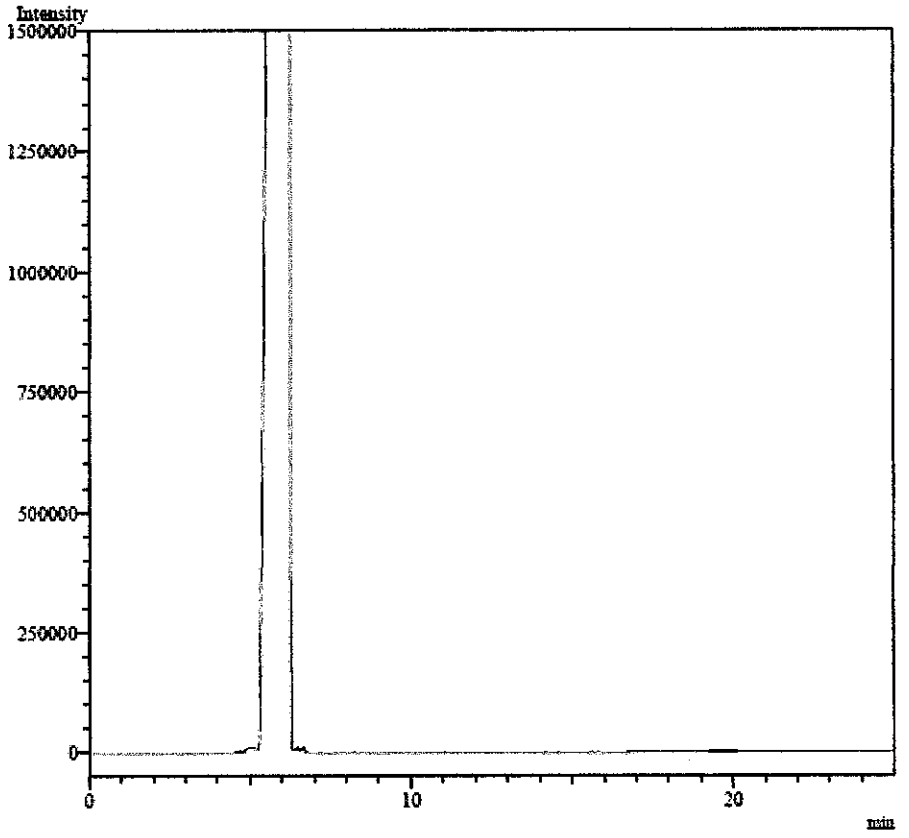
a) EMIM DEP-SiO_2

Sample Information

Analysis Date & Time : 04/07/2012 3:24:44 PM

Sample Name : sample a
Sample ID :

Data Name : C:\GCsolution\Data\2012\madihah\madihah 01.gcd
Method Name : C:\GCsolution\Data\hasiah\madihah\calib curve HA in Dodecane_maddy.gcm



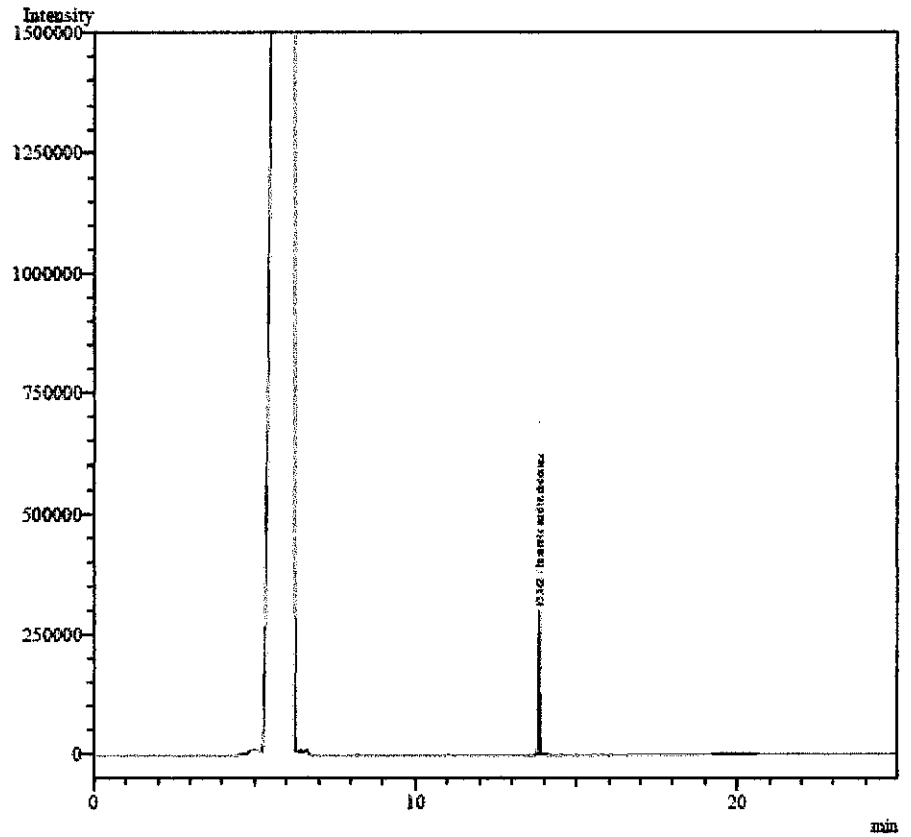
b) BMIM DCN-SiO_2

Sample Information

Analysis Date & Time : 04/07/2012 3:54:38 PM

Sample Name : sample b
Sample ID :

Data Name : C:\GCsolution\Data\2012\madihah\madihah 02.gcd
Method Name : C:\GCsolution\Data\hasiah\madihah\calib curve HA in Dodecane_maddy.gcm



Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	13.863	717291.25	300225.24	0.631	wt%	hexanoic acid in
Total		717291.25		0.631		

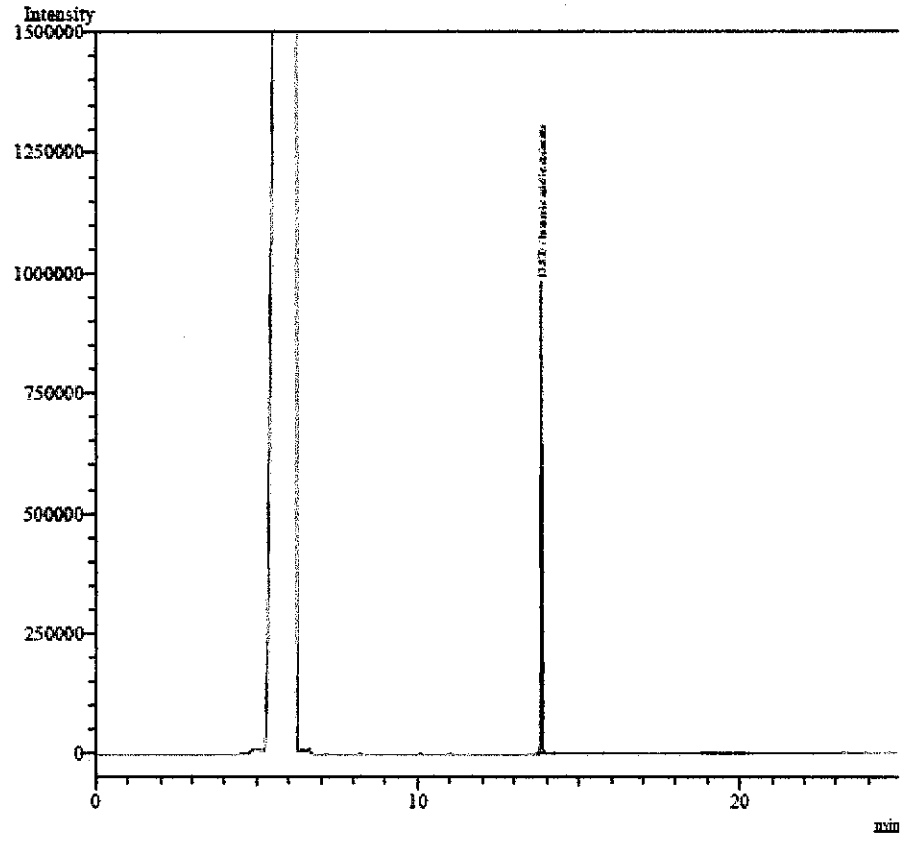
c) BMIM OTF-SiO_2

Sample Information

Analysis Date & Time : 04/07/2012 4:26:59 PM

Sample Name : sample c
Sample ID :

Data Name : C:\GCsolution\Data\2012\madihah\madihah 03.gcd
Method Name : C:\GCsolution\Data\hasiah\madihah\calib curve HA in Dodecane_maddy.gcm



Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	13.870	2340882.40	980098.57	2.058	wt%	hexanoic acid in
Total		2340882.40		2.058		

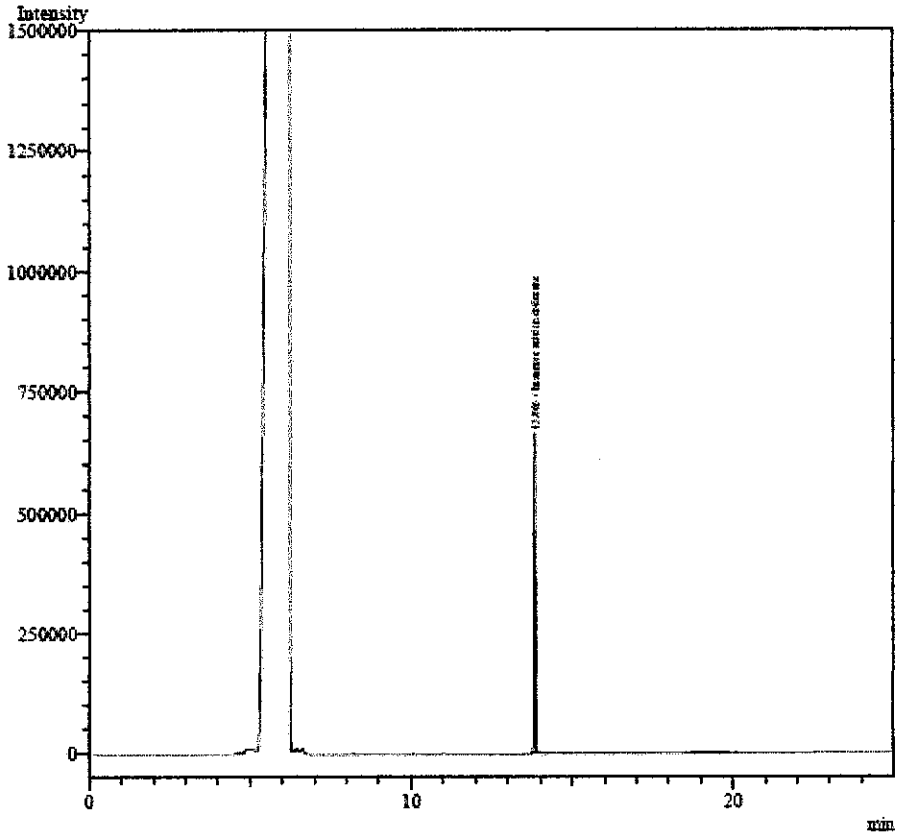
d) BMIM $MeSO_4$ –SiO_2

Sample Information

Analysis Date & Time : 04/07/2012 4:56:54 PM

Sample Name : sample d
Sample ID :

Data Name : C:\GCsolution\Data\2012\madihah\madihah 04.gcd
Method Name : C:\GCsolution\Data\hasiah\madihah\calib curve HA in Dodecane_maddy.gcm



Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	13.866	1576890.22	661761.50	1.386	wt%	hexanoic acid in
Total		1576890.22		1.386		

Hexanoic Acid Extraction (Multiple Stages):

a) First Stage

Sample Information

Analysis Date & Time : 02/08/2012 12:58:26 PM

Sample Name : sample HA 1
Sample ID :

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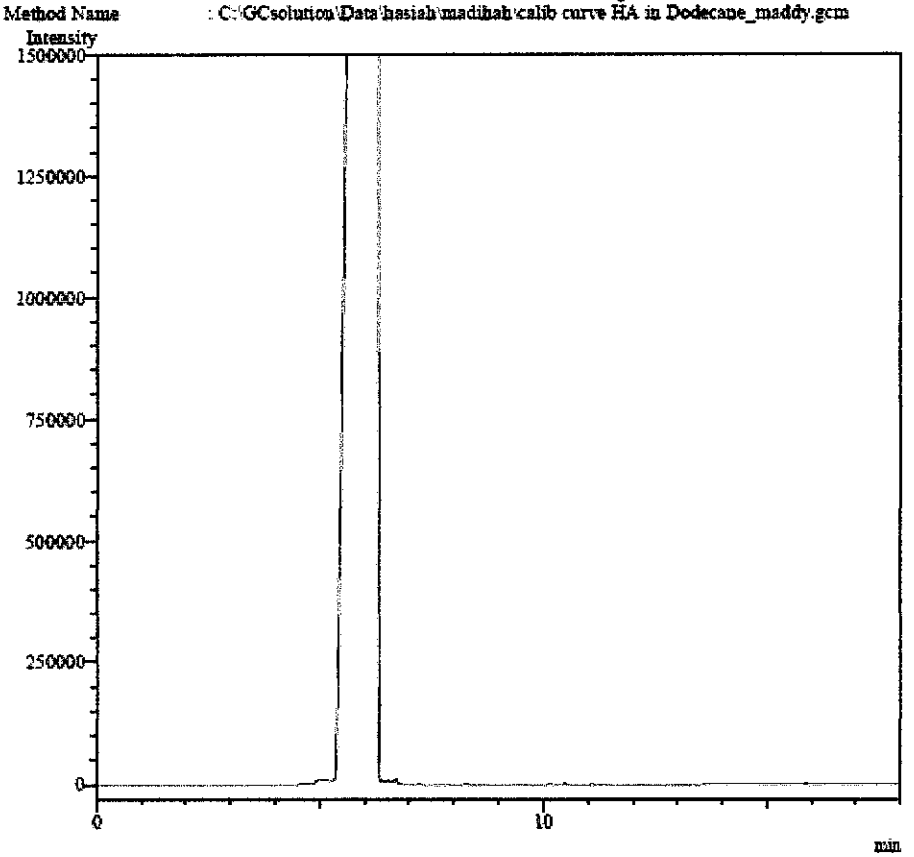
Method Name : C:\GCsolution\Data\hasiah\madihah\calib curve HA in Dodecane_maddy.gcm



b) Second Stage

Sample Information

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Sample Name : sample HA 2
Sample ID :

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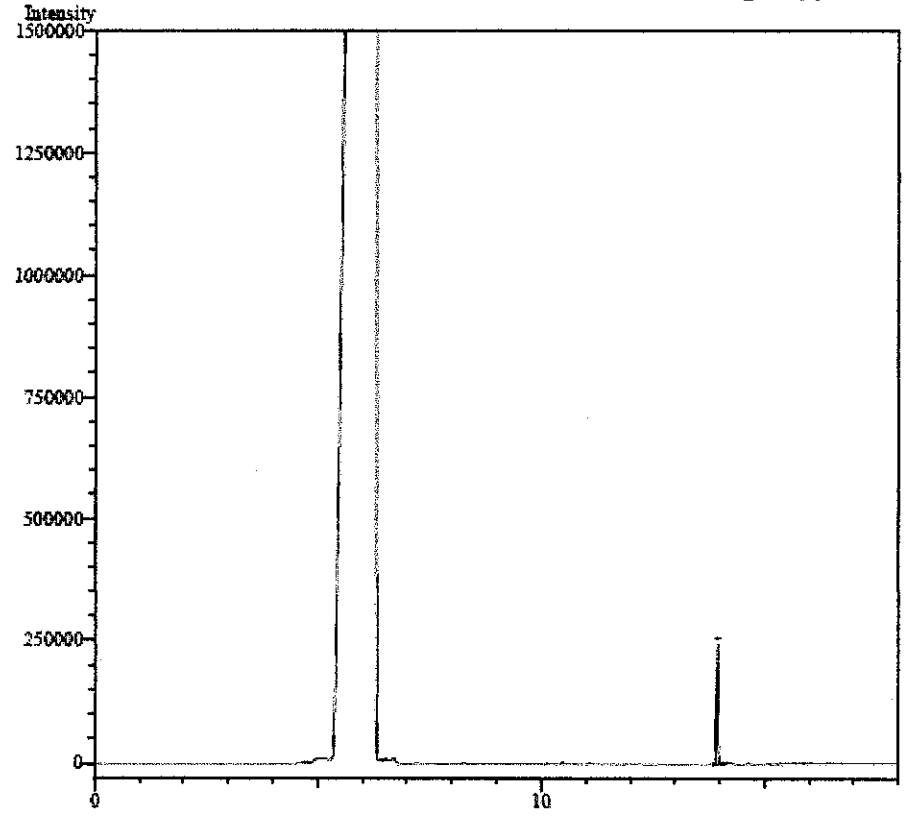

Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	13.938	583492.06	242670.94	0.5130	wt%	hexanoic acid in dodecane
Total		583492.06		0.5130		

c) Third Stage

Sample Information

Analysis Date & Time : 02/08/2012 1:58:23 PM

Sample Name : sample HA 3
Sample ID :

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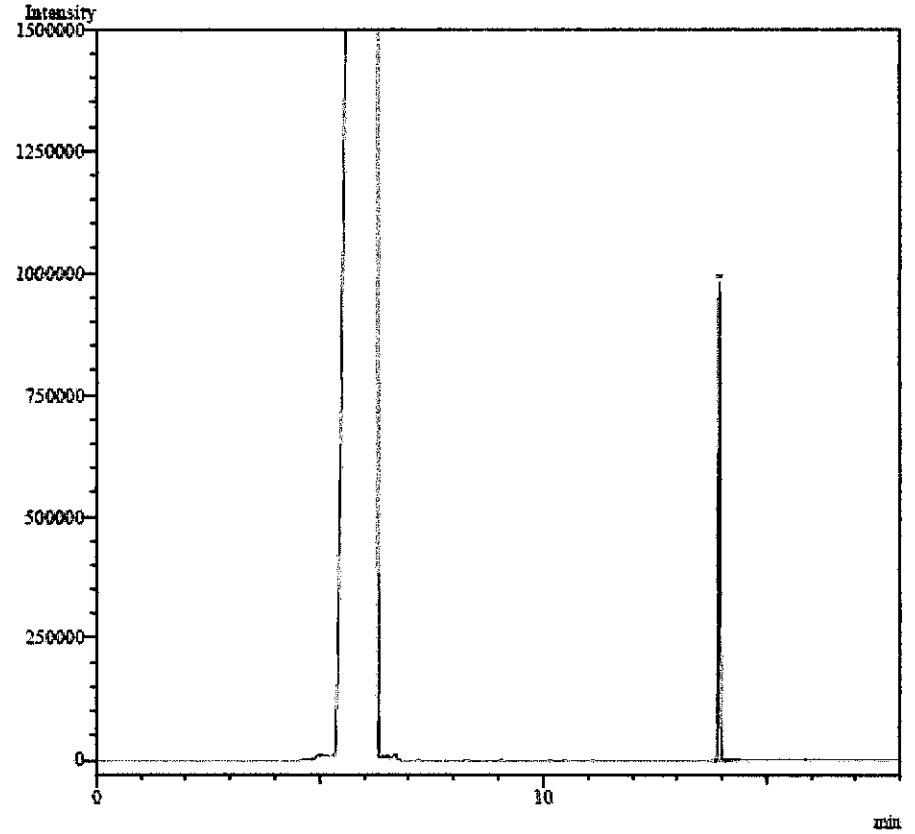

Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	13.943	2340122.32	978468.46	2.0574	wt%	hexanoic acid in dodecane
Total		2340122.32		2.0574		

d) Forth Stage

Sample Information

Analysis Date & Time : 02/08/2012 2:28:20 PM

Sample Name : sample HA 4
Sample ID :

Data Name : C:\GCsolution\Data\2012\madihah\madihah 204.gcd
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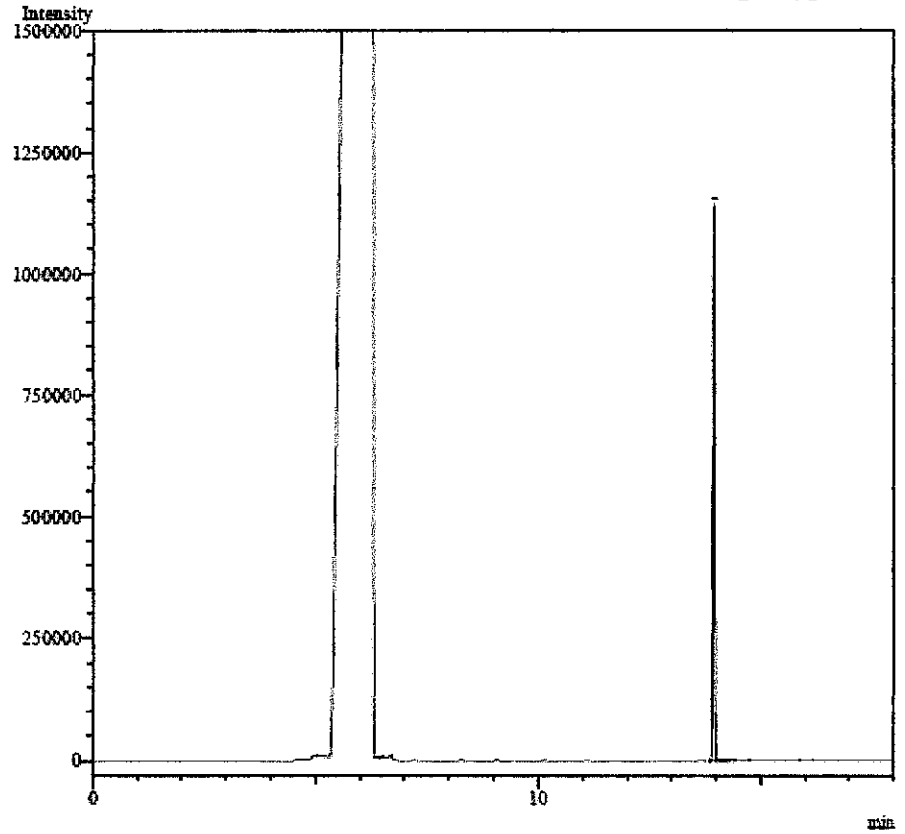


Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	13.946	2786377.97	1141353.47	2.4498	wt%	hexanoic acid in dodecane
Total		2786377.97		2.4498		

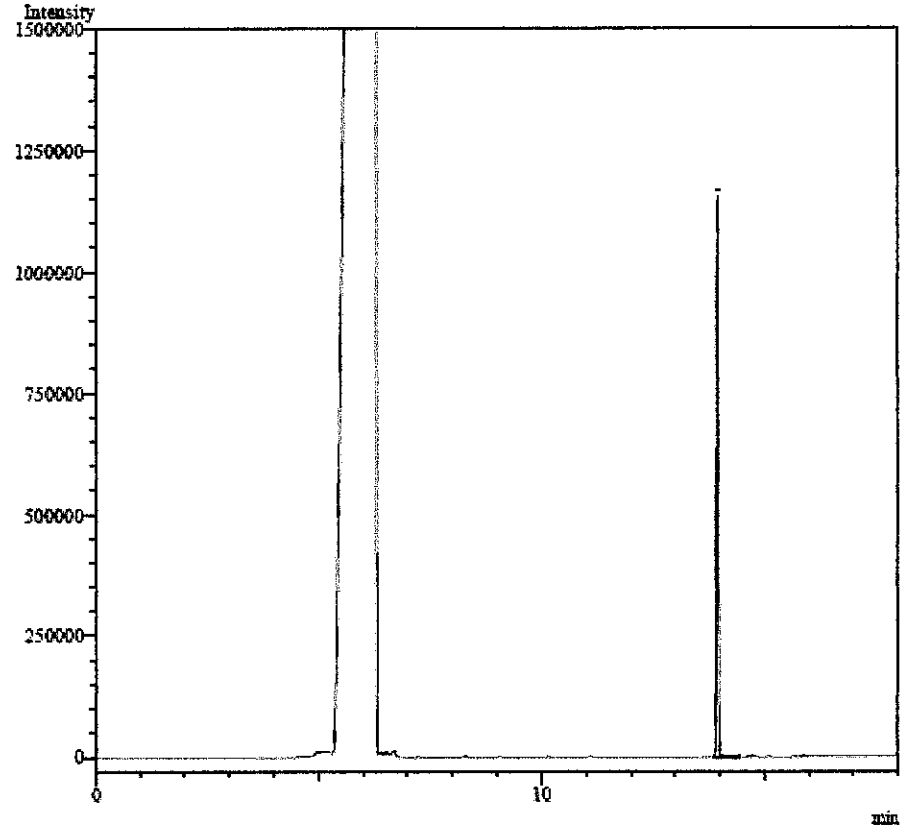
e) Fifth Stage

Sample Information

Analysis Date & Time : 02/08/2012 2:58:18 PM

Sample Name : sample HA 5
Sample ID :

Data Name : C:\GCsolution\Data\2012\madihah\madihah 205.gcd
Method Name : C:\GCsolution\Data\hasiah\madihah\calib curve HA in Dodecane_maddy.gcm



Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	13.946	2794045.85	1153578.48	2.4565	wt%	hexanoic acid in dodecane
Total		2794045.85		2.4565		

Benzoic Acid Extraction (Multiple Stages):

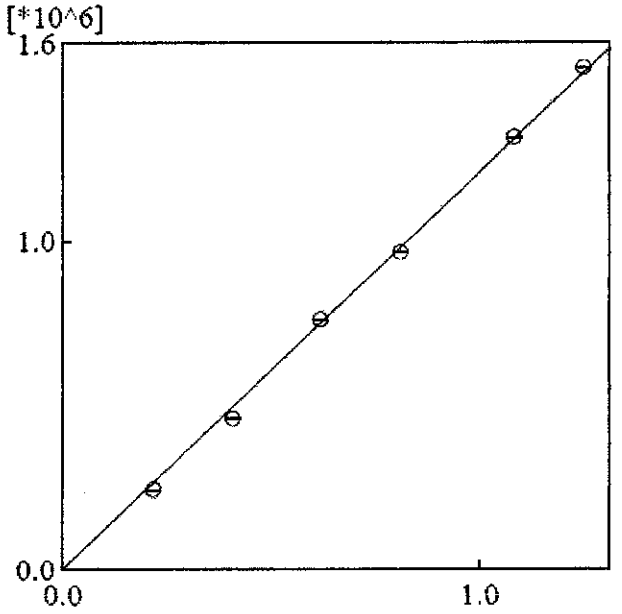
a) BA Calibration Curve

Calibration Curve - Analytical Line 1 - Channel 1

ID#:1 Name:benzoic acid in dodecane

f(x)=1210233.05031*x+0.0
R=0.999613041993 R^2=0.999226233722
MeanRF:1179648.4335 RFSD:54919.0318321 RFRSD:4.65554230164
CurveType:Linear
ZeroThrough:Weight on Origin
WeightedRegression:None

External Standard



No.	Conc.	Area
1	0.218	240879
2	0.408	455472
3	0.620	759573
4	0.810	965600
5	1.084	1316919
6	1.249	1527874

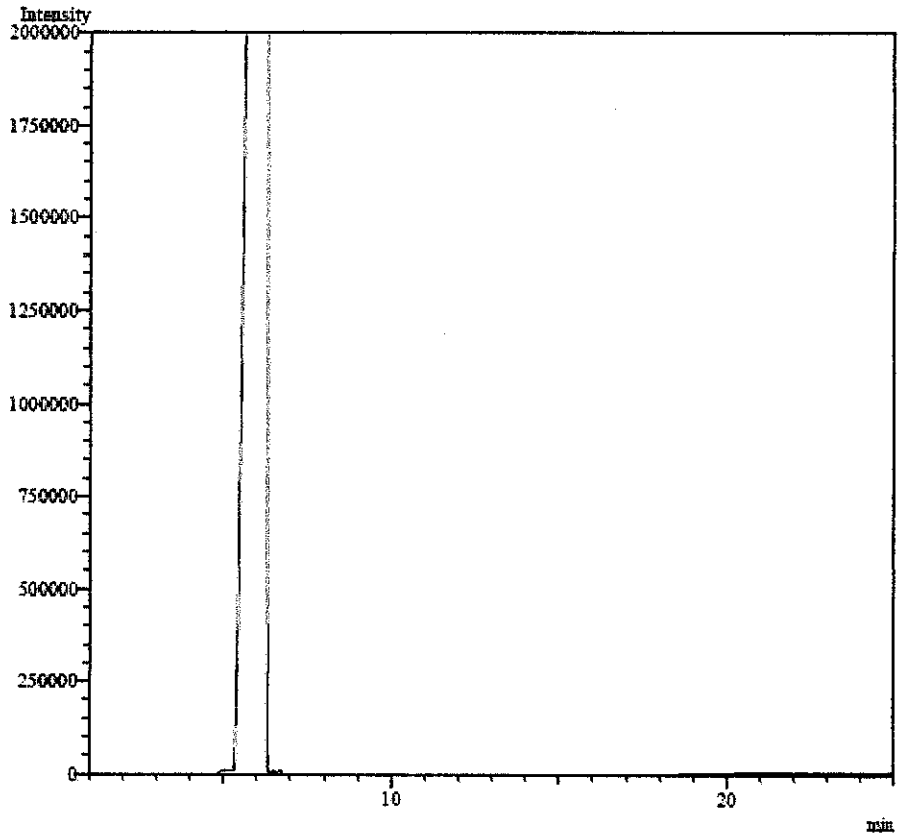
b) First Stage

Sample Information

Analysis Date & Time : 20/07/2012 12:39:38 AM

Sample Name : EMIMDEP_MS1BA
Sample ID :

Data Name : E:\YUTP\EMIMDEP_MS1BA.gcd
Method Name : C:\GCsolution\Data\hasiah\madihah\calib curve BA in Dodecane_maddy.gcm



c) Second Stage

Sample Information

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Sample ID :

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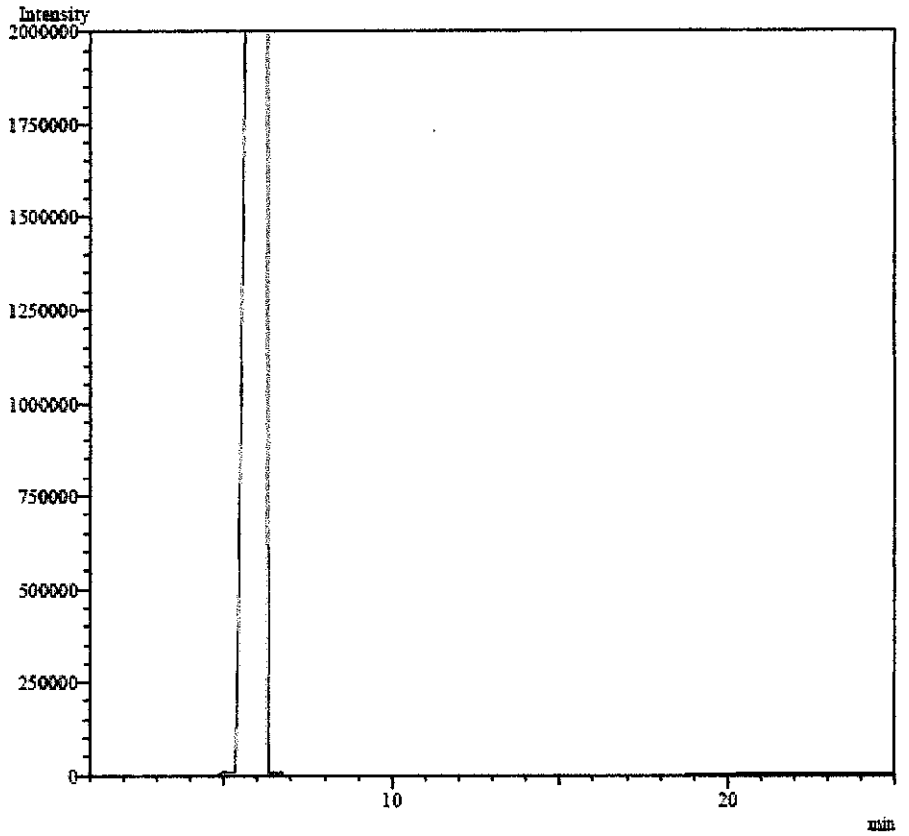
Method Name : C:\GCsolution\Data\hasiah\maslihah\calib curve BA in Dodecane_maddy.gcm



d) Third Stage

Sample Information

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Sample ID :

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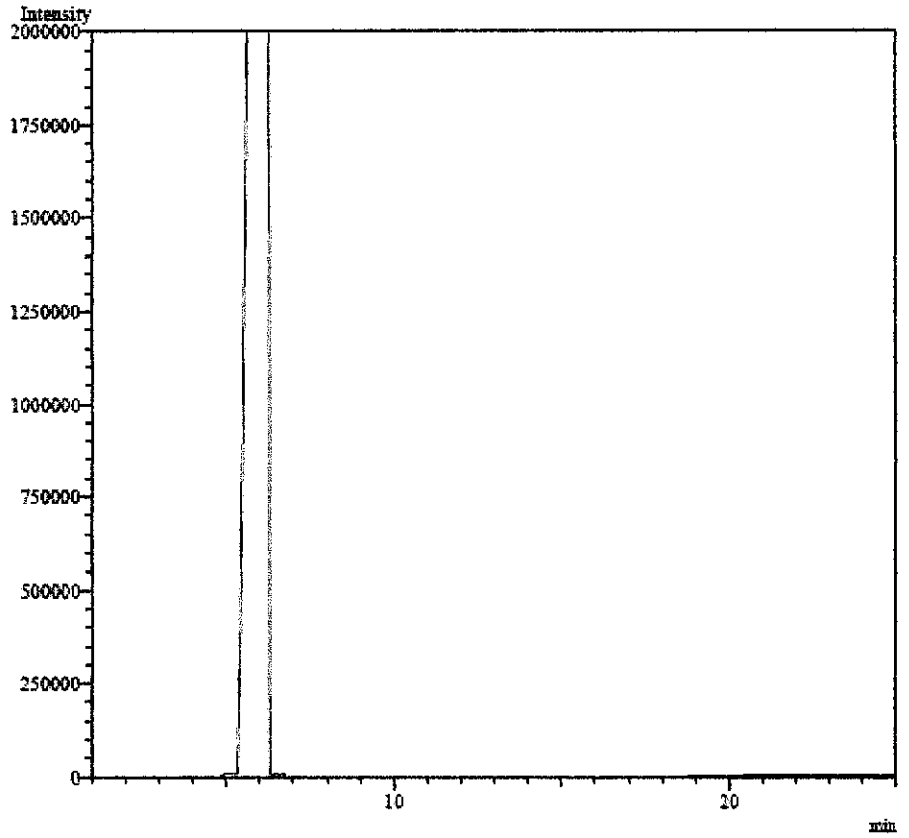
Method Name : C:\GCsolution\Data\hasiah\madihah\calib curve BA in Dodecane_maddy.gcm



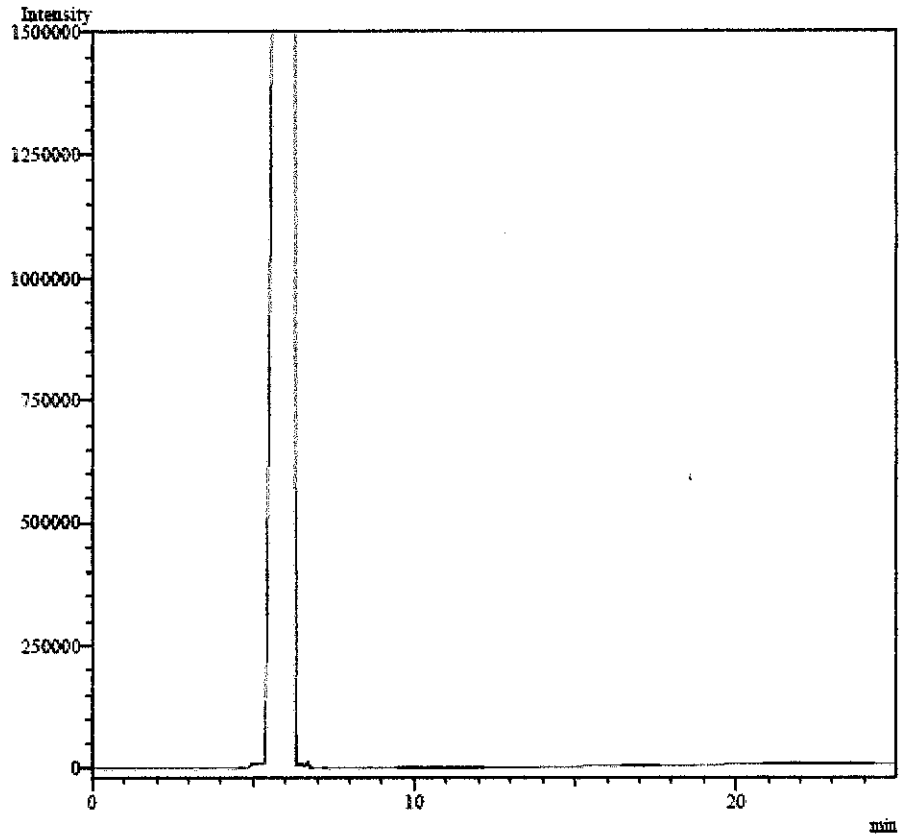
e) Forth Stage

Sample Information

Analysis Date & Time : 20/07/2012 10:33:52 AM

Sample Name : EMIMDEP_BA MS4
Sample ID :

Data Name : E:\gc 03\EMIMDEP_MS4BA.gcd
Method Name : C:\GCsolution\Data\hasiah\madihah\calib curve BA in Dodecane_maddy.gcm



f) Fifth Stage

Sample Information

Analysis Date & Time : 20/07/2012 11:03:47 AM

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Sample ID :

Data Name : C:\GCsolution\Data\2011\ashfaq\EMIMDEP_M55BA.gcd
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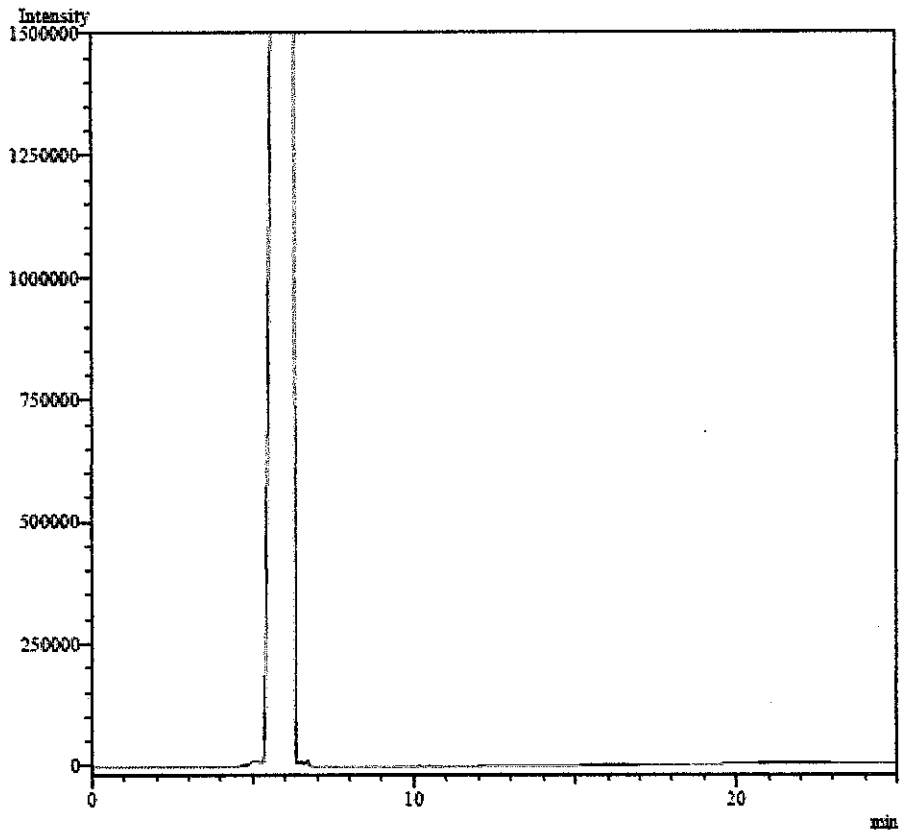
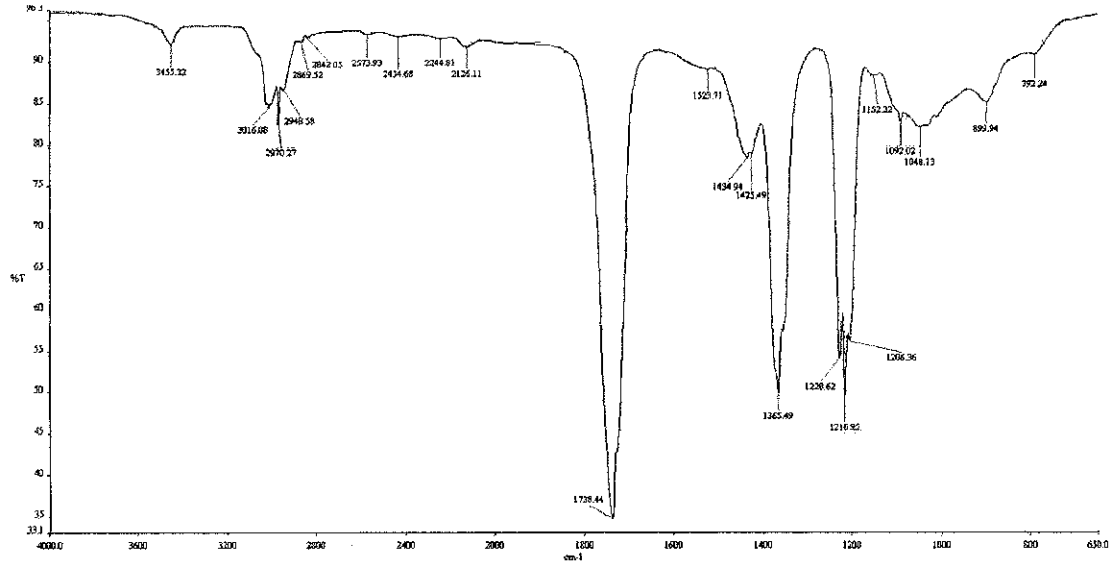
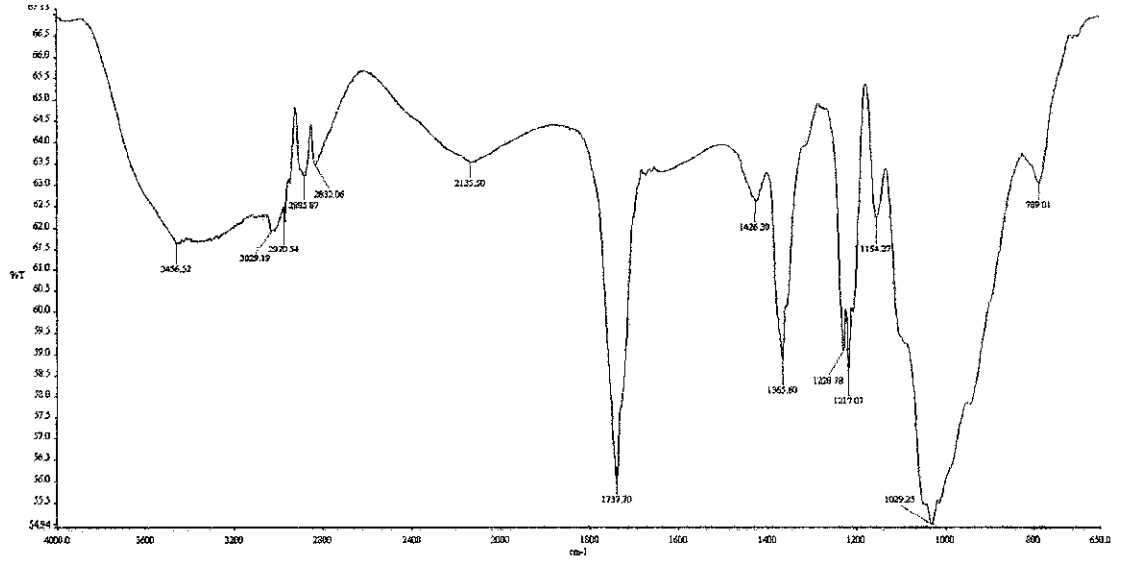


APPENDIX B - FTIR

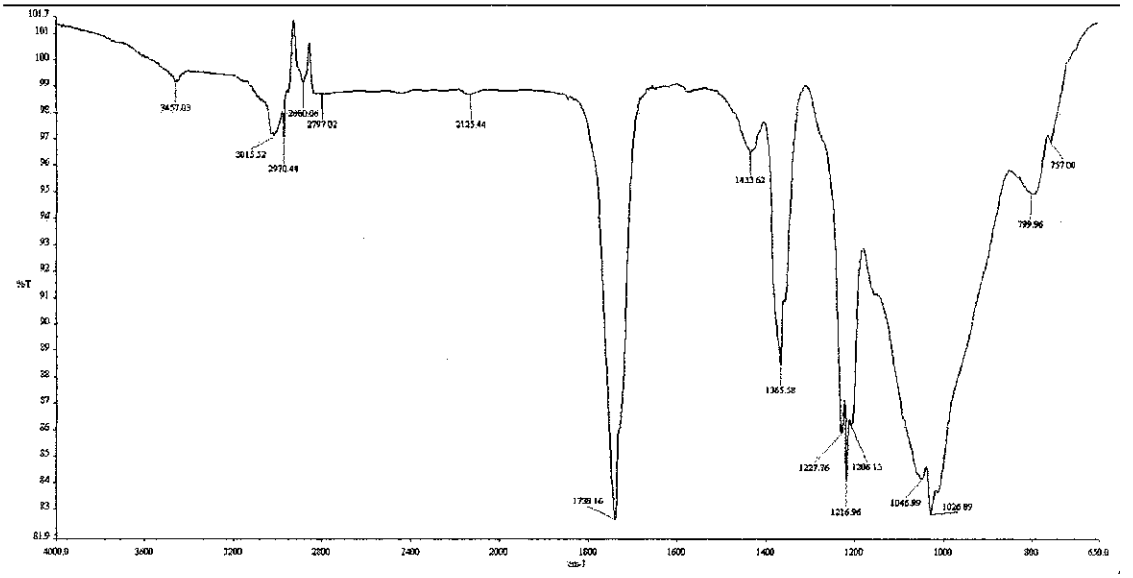
a) Calcined Commercial Silica 0.063 mm



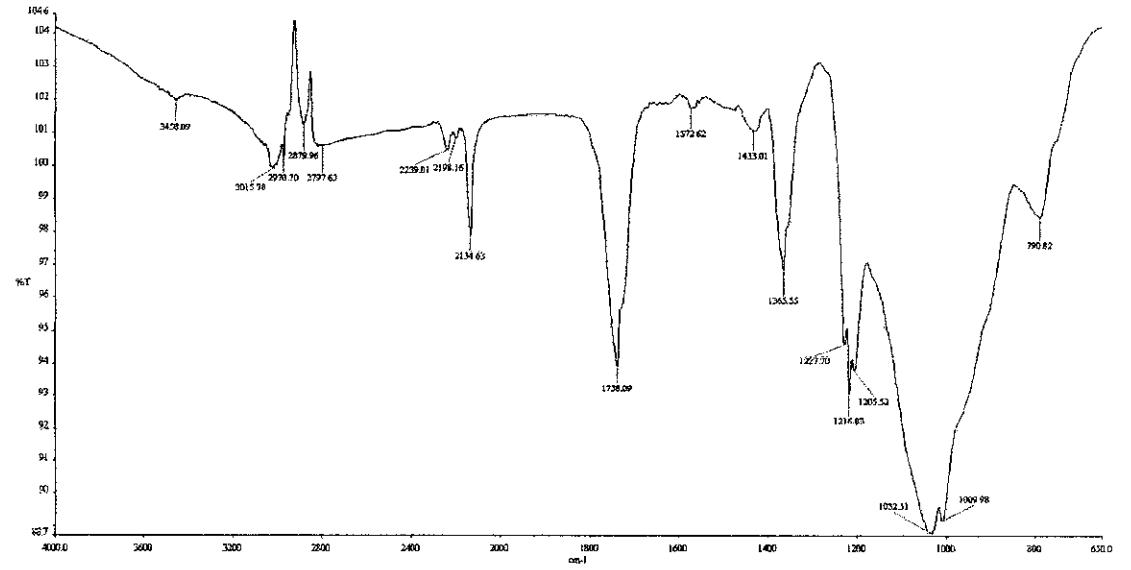
b) EMIM DEP-SiO_2



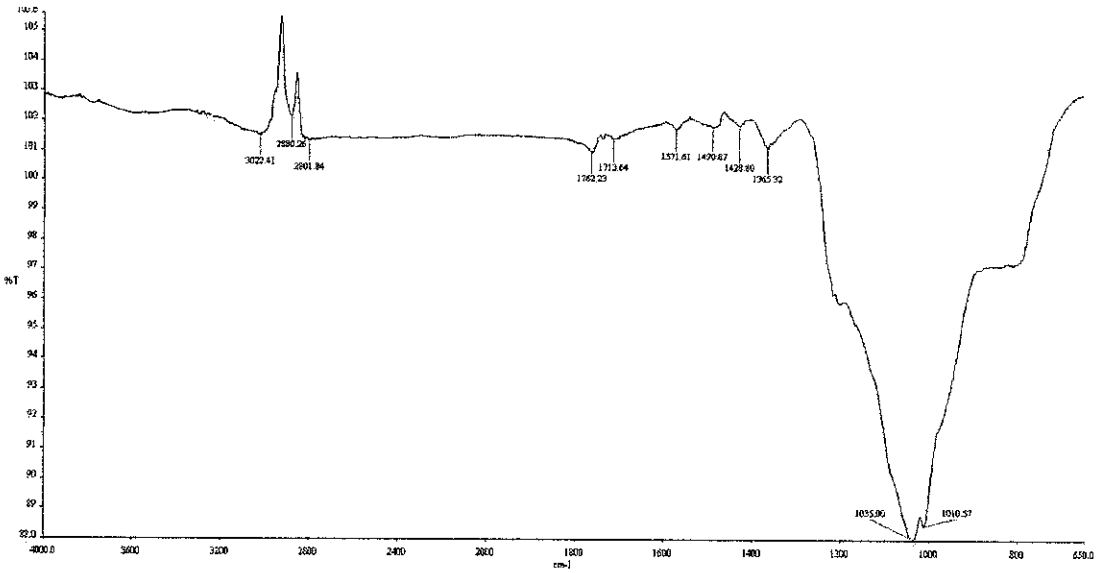
c) BMIM OTF-SiO_2



d) BMIM DCN-SiO_2

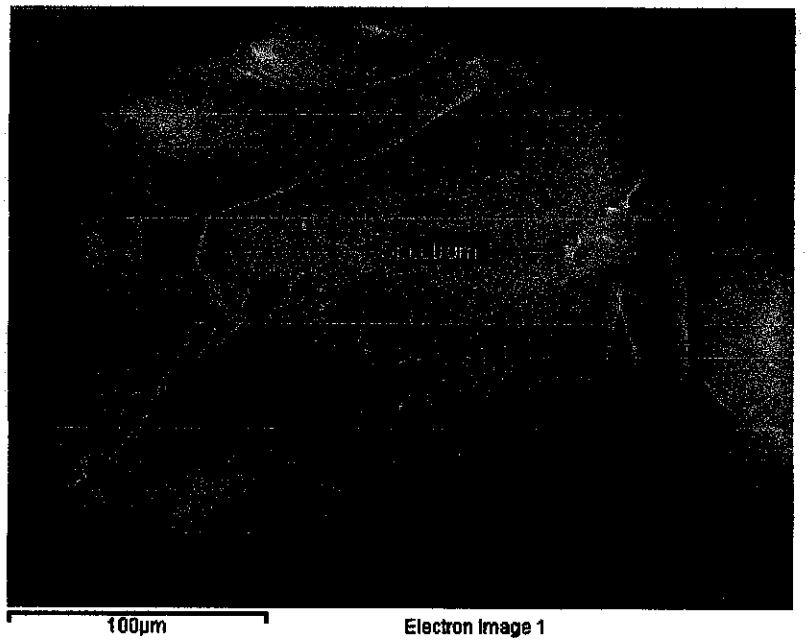


e) BMIM $MeSO_4$-SiO_2



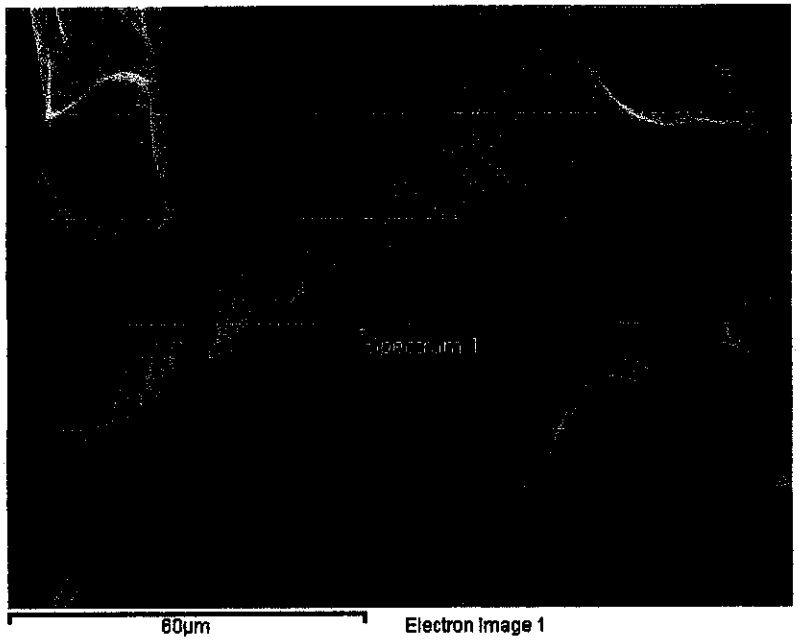
APPENDIX C – EDX

a) Commercial Silica 0.063 mm



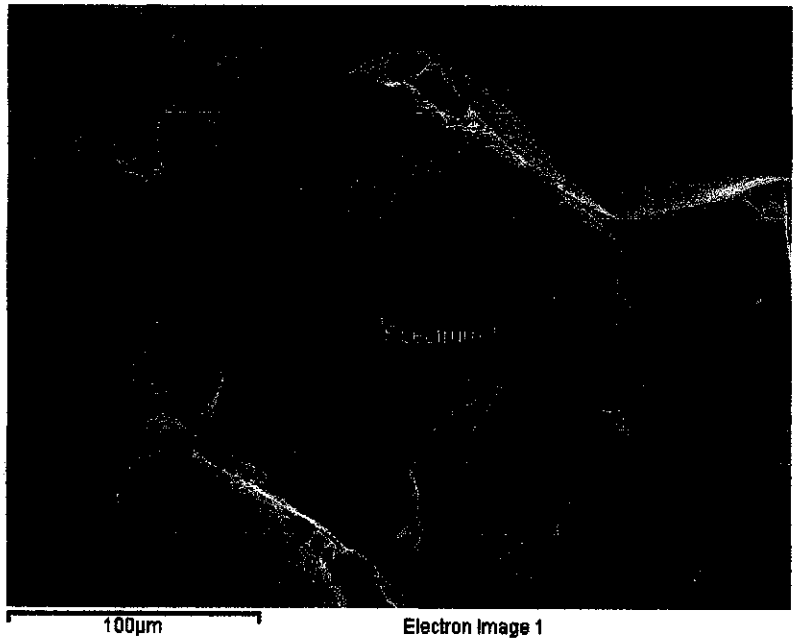
Element	Weight%	Atomic%
C K	10.87	15.97
O K	59.12	65.18
Si K	30.01	18.85
Totals	100.00	

b) EMIM DEP-SiO_2



Element	Weight%	Atomic%
C K	26.33	36.32
O K	45.84	47.47
Si K	24.15	14.24
P K	3.68	1.97
Totals	100.00	

c) BMIM OTF-SiO_2



Element	Weight%	Atomic%
C K	23.10	32.65
O K	38.01	40.33
F K	13.15	11.75
Si K	22.01	13.30
S K	3.73	1.97
Totals	100.00	